Outlines of Quantitative Analysis

INCLUDING EXAMPLES OF

Analysis of Simple Minerals and Mineral Products.

BY

WILLIAM ROBERT LANG, D.Sc., (Glasgow): F.I.C.
Professor of Chemistry in the University of Toronto.
Formerly Lecturer in the University of Glasgow.

AND

ALFRED TINGLE, B.Sc., (Aberdon. *et* Lond.): Ph.D., (University of Pennsylvania).
Formerly Chemist to the Pei Yang Mint, and to the Bureau of Mines, Chili Province, China.

University Press
Toronto
1911

QE131
.Z6
1
***

PART I.

OUTLINES OF QUANTITATIVE ANALYSIS.

Part I. was written some time ago as a systematic guide for students in the laboratory of the University of Toronto and has already been published under the title *Outlines of Qualitative and Quantitative Analysis*, (W. R. Lang, University Press, 1910). The methods described are all standard ones and too well known to require specific acknowledgment of their original sources.

In Part II., while recognising that it is undesirable to overburden the text of a book of this class with references to original articles, the insertion of some seemed frequently called for and where this was so we have not hesitated to give them. The student is strongly advised to consult these references and to follow on from them to others, as his outlook on Analytical Chemistry will be greatly broadened by so doing.

We wish to acknowledge our indebtedness to W. F. Hillebrand's *Analysis of Silicates and Carbonate Rocks* (*U.S. Geological Survey, Bull. No. 303*). For the analysis of Coal, the procedure given is similar to that recommended in the *Report of the American Chemical Society's Committee on Coal Analysis*, (*Journal, vol. XX.*). Our thanks are also due to Professor W. A. Noyes for his kindness in privately calling our attention to the merits of the gravimetric method for determining Manganese in Spiegel, described in **183.**

The electrolytic methods given in the text do not include any which call for the use of mercury cathodes, rotating electrodes or more recent elaborations: descriptions of these will be found in the journals or in such text books as Edgar F. Smith's *Electro Analysis*. To the latter we would also refer the student for information on such matters as sources of current, construction of rheostats and the choice of electrical measuring instruments.

The authors will be grateful if defects or mistakes are brought to their notice.

TORONTO,
MARCH, 1911.

CONTENTS.

PART I.

Page.
Principles of Analysis 1

VOLUMETRIC METHODS.

Standard Solutions and Measuring Instruments 2
Normal and Decinormal Solutions 3
Methods based on Neutralisation:—
  i. Alkalimetry 5
  ii. Acidimetry 7
  iii. Indirect applications of these 7
Methods based on Oxidation:
  Standard Potassium Permanganate 8
  Determination of Iron in a Ferrous salt 9
  " " " Ferric salt 10
  " " in Ferrous and Ferric salts when mixed 10
  Standardisation of Potassium Permanganate 10
  Determination of Oxalic Acid and Oxalates 11
  " " Bases yielding insoluble Oxalates 11
  Standard Potassium Bichromate and its applications 12
  Standard Iodine Solution 13
  Standard Sodium Thiosulphate 13
  Direct titrations with standard Iodine 14
  Uses of Iodine and Thiosulphate 15
Methods based on Precipitation:—
  Standard Silver Nitrate and its applications 15
Miscellaneous Methods:—
  Determination of "Available Chlorine" in Bleaching Powder 17
  Determination of Nitrogen by Kjeldahl's method:
    (*a*) No Nitrates present 18
    (*b*) In the presence of Nitrates 20

GRAVIMETRIC METHODS.

Solution, Evaporation, Filtration: Washing, Drying, and Ignition of Precipitates 21
Determination of Iron 23
  " " Aluminum 24
  " " Chromium 24
  " " Copper 24
  " " Sulphuric Acid 24
  " " Lead 25
  " " Magnesium 25
  " " Calcium 26
  " " Phosphoric Acid 26
  " " Copper and Iron when mixed 26
  " " Carbon Dioxide, by difference 27
  " " " " by direct weighing 28

PART II.

THE ANALYSIS OF SIMPLE MINERALS AND MINERAL PRODUCTS.

  Limestone 31
  Clays 33
  Haematite 37
  Coal 42
  Calorimetry 43
  Copper Matte 45
  Pyrites 48
  Nickel-Steel 50
  Iron 50
  Technical method for examining Pig Iron, Cast Iron, Steel 53
  Spiegel-Eisen and Manganese ores 54
  Tourmaline 55
Table of International Atomic Weights 57
Index 5

QUANTITATIVE ANALYSIS.

The instructions contained in the author's *Outline of Qualitative Analysis* are intended to familiarise the student with the appearance and properties of substances and by means of this knowledge to determine of what a substance is composed, *i.e.*, what metal or metals are contained in it and what acid radicle or radicles. In the following pages is given a short and concise account of how the *amounts* of these bodies are estimated, in other words, an introduction to quantitative anlysis. It can not be too strongly impressed on the student at this stage the absolute necessity of orderly and methodical work, complete precipitation, complete washing of precipitates and all-round cleanliness in manipulation; the loss of one drop of a solution adhering to a beaker may occasion an error of several per cent. The student should also enter in his note book the details of each operation as it is done and not wait to "write it up" afterwards. The laboratory note-book must be kept in such a way that reference to previous work can readily be made.

1. There are two great principles on which the quantitative determination of substances is based, GRAVIMETRIC and VOLUMETRIC. In gravimetric analysis the element to be estimated is converted into a stable and, in most cases, insoluble compound, usually by precipitation under proper conditions with some reagent or reagents, and this precipitate *of known composition* accurately weighed. From this is calculated the amount of the substance under examination. For example, the amount of silver in an alloy is wanted: a weighed portion of the alloy is therefore dissolved in nitric acid and the silver precipitated by hydrochloric acid as chloride (***AgCl***). This precipitate is washed, dried, fused in a porcelain crucible and weighed; from this weight is calculated the amount of silver present. Conversely, chlorine is estimated by precipitation with silver nitrate. In like manner—

To estimate	Barium,	convert it into	$BaSO_4$,	ignite this precipitate and weigh as	$BaSO_4$.
" "	Sulphur,	" "	$BaSO_4$,	" " " " "	$BaSO_4$.
" "	Aluminium,	" "	$Al(OH)_3$,	" " " " "	Al_2O_3.
" "	Iron,	" "	$Fe(OH)_3$,	" " " " "	Fe_2O_3.
" "	Chromium,	" "	$Cr(OH)_3$,	" " " " "	Cr_2O_3.
" "	Copper,	" "	$Cu(OH)_2$,	" " " " "	CuO.
" "	Magnesium,	" "	$MgNH_4PO_4$,	" " " " "	$Mg_2P_2O_7$.
" "	Phosphorus,	" "	$MgNH_4PO_4$,	" " " " "	$Mg_2P_2O_7$.
" "	Arsenic,	" "	$MgNH_4AsO_4$,	" " " " "	$Mg_2As_2O_7$.
" "	Calcium,	" "	CaC_2O_4,	" " " " "	CaO.
" "	Chlorine,	" "	$AgCl$	" " " " "	$AgCl$.
" "	Tin,	" "	SnS,	" " " " "	SnO_2
" "	Nickel,	" "	$Ni(OH)_2$,	" " " " "	NiO.
" "	Lead,	" "	$PbSO_4$,	" " " " "	$PbSO_4$.
" "	Manganese,	" "	$MnCO_3$,	" " " " "	Mn_3O_4.
" "	Zinc,	" "	ZnS, ignite in an atmosphere of hydrogen and weigh as		ZnS.
" "	Cobalt,	" "	$Co(OH)_2$,	" " " " "	Cobalt.
" "	Antimony	" "	Sb_2S_3,	ignite with nitric acid and weigh as	Sb_2O_4.
" "	Cadmium,	" "	CdS,	and weigh in this form on a tared filter.	
" "	Mercury,	" "	HgS,	" " " " " "	
" "	Potassium,	" "	$PtCl_4 2KCl$,	" " " " " "	
" "	Ammonium,	" "	$PtCl_4 2NH_4Cl$,	" " " " " "	
" "	Carbonic acid, absorb it in a weighed amount of potassium hydrate.				

2. In order to ascertain the amount of the element or acid radicle that corresponds to the compound weighed, the weight of such precipitate is multiplied by a factor (which the student should obtain for himself) whose denominator is the formula-weight of the compound and whose numerator is the number representing the weight of that element or acid radicle contained in it. For example; a barium sulphate precipitate weighed 2.5 grams, the weight of barium contained in this will be $2.5 \times \frac{137}{233}$ grams, there being 137 grams of barium contained in every 233 grams of its sulphate. [$Ba = 137$, $S = 32$, $O_4 = 64$; total $= 233$]. Likewise, if in order to estimate the amount of sulphur contained in a sample of (say) coal. 5 grams of the sample yielded, after suitable treatment, an amount of barium sulphate which, when dried, weighed .25 gram, the 5 grams of coal must have contained $.25 \times \frac{32}{233}$ gram of sulphur, *i.e.*, $\frac{.25 \times 32 \times 100}{233 \times 5}$ per cent.

3. Since the process of precipitating, washing, drying and weighing precipitates occupies considerable time, more expeditious methods are often employed, use being made of solutions of reagents of known strength, and estimations done in this way come under the head of VOLUMETRIC ANALYSIS. In the first of the two examples above, that of the determination of barium, the reaction between a soluble salt of barium and a soluble sulphate may be represented by the equation,

$$\underbrace{\underset{137+2\times35.5}{BaCl_2}}_{208} + \underbrace{\underset{2\times23+32+4\times16}{Na_2SO_4}}_{142} = \mathbf{BaSO_4} + 2NaCl$$

every 142 grams of Na_2SO_4 will *exactly* convert 208 grams of $BaCl_2$ into **$BaSO_4$**. If, then, a solution of sulphate of soda (calculated as the anhydrous salt) be made *of known strength* and carefully run into the solution of barium chloride till it causes no further precipitate, the volume of solution used being known and the amount of sulphate of soda contained in that volume likewise known, from this the quantity of barium chloride present in the solution experimented on is at once ascertained.

4. Such solutions of known strength are called **Standard Solutions:** a known weight of the reagent is dissolved in a definite volume of water and the amount of such reagent contained in each c.c. of the solution is therefore known. Suppose a solution of silver nitrate is made containing .017 gram of the salt in every c.c., this amount (.017 gram) is capable of precipitating .00355 gram of chlorine in the form of silver chloride. If 100 c.c. of a solution of common salt requires 40 c.c. of this silver solution to complete the chemical change represented by the equation $NaCl + AgNO_3 = \mathbf{AgCl} + NaNO_3$, then that volume of sodium chloride solution will contain $40 \times .00355$ grams chlorine, and from this the amount of common salt can be calculated. The process of running a standard solution into the one whose strength is being determined is known as *titration*; in the example given, the salt solution is said to be *titrated* with standard silver nitrate.

5. The instruments used for measuring liquids are—**Graduated Flasks, Cylinders** or **Test-mixers, Pipettes** and **Burettes.** The first are flasks that contain a certain volume of liquid when filled up to a mark cut on the neck. These are of various sizes, from 50 c.c. to 1000 c.c. (1 litre) and the mark is usually placed at such a place that, when filled to that mark, the flask will *contain* the exact number of cubic centimetres that its nominal capacity indicates. It must be remembered that this will not be the amount that it will *deliver* if emptied, for some will necessarily adhere to the walls.

6. Graduated Cylinders, or **Test-mixers** as they are called, are useful for measuring large quantities of liquids.

7. The **Pipette** is a glass tube, usually with a cylindrical bulb in the middle, drawn to a point at its lower end, with a graduation mark indicating its capacity to *deliver* a specified volume of liquid. A pipette should be allowed to empty itself and the last few drops that collect at the narrowed end, after it is held in a perpendicular position for about 15 seconds, blown out. Before filling a pipette with a solution it should, if wet, be washed out with a little of the liquid it is intended to measure. Pipettes vary in capacity from 1 c.c. to 100 c.c.

8. Burettes are graduated almost through their entire length in tenths of a cubic centimetre and the contents are drawn off by a tap at the lower end. A burette should be washed out with the solution it is going to contain before it is finally filled for use.

9. Reading Graduated Instruments. A liquid in a tube has not a plane surface but, owing to capillarity, it has a curved one known as the *meniscus*; in selecting what part of this curve is to be observed in reading the volume of a liquid, it is customary to take the graduation on the tube that corresponds with the *lowest point of the meniscus.*

10. The methods in use in volumetric analysis are based mainly on three classes of reactions, **Neutralisation, Oxidation or Reduction,** and **Precipitation.**

11. Neutralisation of an alkali with an acid and the converse. The former is known as *alkalimetry* and the latter as *acidimetry*. Here the exact amount of "standard solution" required to neutralise the other substance determines the amount of acid or alkali that the sample contains. To know when neutralisation is complete an "indicator" is employed which will give definite and different colours with acids and alkalies; thus the "end-point" of the reaction, for example, when sulphuric acid has converted all of a sample of potassium hydrate into potassium sulphate, will be shown by the indicator which was (say) red with the alkali turning (say) colourless.

12. Oxidation or Reduction. Here the amount of the substance is determined by the quantity of "standard solution" required to change it from a higher state of oxidation to a lower, or *vice-versa*.

13. Precipitation. The simplest example of this is when a "standard solution" of silver nitrate is added to a solution of a chloride giving a precipitate of silver chloride. The reaction is complete, that is, the "end-point" is reached, when the addition of another drop of the reagent causes no further precipitation of silver chloride.

14. Indirect Methods are also often employed. For example, iodine is capable of very accurate determination by "standard solutions" of sodium thiosulphate, and a number of substances can liberate iodine quantitatively from potassium iodide. The amount of such substance can therefore be *indirectly* determined by estimating the *iodine* it has set free. A still more indirect example is the case of chromate of potassium and hydrochloric acid, which under certain conditions yield free chlorine; the free chlorine when passed into a solution of potassium iodide liberates its equivalent of iodine and this last can be determined by titration with thiosulphate. Hence the amount of *chromium* is found.

15. Standard Solutions are solutions of known strength, containing a definite weight of a substance uniformly distributed throughout a definite volume of solvent. Such a solution *may* be made of any strength provided such strength is known. A solution of common salt containing 10 grams in every litre (1000 c.c.) would be a standard solution and each c.c. would contain .01 gram salt which would be capable of precipitating .0184 gram silver as chloride, for, $\underbrace{\underset{108+14+48}{AgNO_3}}_{170} + \underbrace{\underset{23+35.5}{NaCl}}_{58.5} = AgCl + NaNO_3$, *i.e.*, 58.5 grams salt will convert 108 grams of silver into silver chloride and consequently .01 gram will precipitate $\frac{108 \times .01}{58.5} = .0184$ gram of silver.

16. But it is customary to make standard solutions of such a strength that one solution will be comparable with another, that is to say that the quantities of the *active constituents* in such solutions will be proportional to their chemical equivalents. Standard solutions, therefore, of common salt and of silver nitrate—(the example used above might be called an *empirical* standard solution)—will contain in a litre 35.5 grams of chlorine and 108 grams of silver respectively. So, taking one litre as the volume in which the substances are contained, standard solutions of hydrochloric acid, sulphuric acid, nitric acid, sodium hydrate, and potassium carbonate, will contain 1, 1, 1, 23, and 39 grams of hydrogen, of sodium and of potassium respectively. Such solutions are called **Normal Solutions** and a normal solution may be defined as *one containing the chemical equivalent of one gram of hydrogen per litre.*

17. For example :

Normal	HCl,	(molecular wt.	1 + 35.5,	*i.e.*,	36.5)	contains	36.5	grams	per	litre.
″	HNO_3,	(″ ″	1 + 14 + 48,	″	63)	″	63	″	″	″
″	KHO,	(″ ″	39.1 + 1 + 16,	″	56.1)	″	56.1	″	″	″
″	$NaHO$,	(″ ″	23 + 1 + 16,	″	40)	″	40	″	″	″
″	H_2SO_4,	(″ ″	2 + 32 + 64,	″	98)	″	$\frac{98}{2}$	″	″	″
″	H_3PO_4,	(″ ″	3 + 31 + 64,	″	98)	″	$\frac{98}{3}$	″	″	″
″	Na_2CO_3,	(″ ″	46 + 12 + 48,	″	106)	″	$\frac{106}{2}$	″	″	″
″	$AgNO_3$,	(″ ″	108 + 14 + 48,	″	170)	″	170	″	″	″
″	$HC_2H_3O_2$,	(″ ″	4 + 24 + 32,	″	60)	″	60	″		

In the case of acids it will be seen that the quantities required for one litre of normal solutions are those that contain 1 gram of replaceable hydrogen; in the examples of salts given—potassium and sodium hydrates, sodium carbonate and silver nitrate, *the chemical equivalents of 1 gram of hydrogen* are potassium (39.1), sodium (23) and silver (108); quantities of these salts therefore, are taken which will contain these amounts of their respective *active* constituents, which, in these cases, are the elements themselves. Solutions will be met with later on in which a *portion* only and not the whole of some particular element takes part in the reaction for which it is used and these cases will be considered and explained as they occur.

18. It will be seen from what has been said that any volume of a normal solution of an acid will be exactly neutralised by the *same* volume of a normal alkali. This will be made clearer by the following equations which represent the reactions that take place between the commoner acids and bases:

(a) $HCl + KHO = KCl + H_2O$

(b) $2HCl + Na_2CO_3 = 2NaCl + H_2O + CO_2$

(c) $H_2SO_4 + 2NaHO = Na_2SO_4 + 2H_2O$

(d) $H_2SO_4 + Na_2CO_3 = Na_2SO_4 + H_2O + CO_2$

(e) $KHO + HC_2H_3O_2 = KC_2H_3O_2 + H_2O$

From these equations it is evident that 56.1 grams KHO, 40 grams NaHO, 53 grams Na_2CO_3, will neutralise 36.5 grams HCl, 63 grams HNO_3, 49 grams H_2SO_4, 60 grams $HC_2H_3O_2$, and, as these are the amounts contained in one litre of a normal solution of each, it follows that a litre or any fraction thereof of a normal alkali will exactly neutralise a litre or the same fraction thereof of any normal acid. So, therefore, if a litre of normal KHO was found to exactly neutralise a quantity of hydrochloric acid, this acid solution must have contained 36.5 grams HCl. Similarly, if a sample of dilute sulphuric acid required 80 c.c. of normal KHO (or normal NaHO, or normal Na_2CO_3) to neutralise it, it must have contained 80 × .049 grams H_2SO_4, each c.c. of normal alkali being capable of neutralising .049 gram H_2SO_4.

19. Standard acids are used for determining alkalies and *vice-versa*, but *normal* solutions are seldom employed being too concentrated to admit of accurate work. Some fraction of normal, as *half-normal*, or *decinormal*, or *centinormal* is more often used and the expressions $\frac{N}{2}$, $\frac{N}{10}$, $\frac{N}{100}$ indicate these strengths. An $\frac{N}{10}$ solution of hydrochloric acid will thus contain 3.65 grams HCl per litre and each c.c. will contain .00365 gram HCl. From the equations given it will be seen that this amount (1 c.c.) of hydrochloric acid is capable of neutralising .0056 gram potassium hydrate, .004 gram sodium hydrate, .0053 gram sodium carbonate, etc., and that 1 c.c. of decinormal sulphuric, nitric and acetic acids can also neutralise these amounts of the alkalies named. Conversely, 1 c.c. of any decinormal alkali will neutralise .00365 gram HCl, .0049 gram H_2SO_4, .0063 gram HNO_3, .006 gram $HC_2H_3O_2$.

20. As these standard solutions are continually being used for determining the amounts of free acid or alkali in solutions they may be conveniently summarised as follows.*

$\frac{N}{10}$ HCl

1 c.c. = .00365 gram HCl
= .0056 " KHO
= .0040 " NaHO
= .0053 " Na_2CO_3
= .0017 " NH_3

$\frac{N}{10}$ KHO

1 c.c. = .0056 gram KHO
= .00365 " HCl
= .0049 " H_2SO_4
= .0063 " HNO_3
= .0060 " $HC_2H_3O_2$

$\frac{N}{10}$ H_2SO_4

1 c.c. = .0049 gram H_2SO_4
= .0056 " KHO
= .0040 " NaHO
= .0053 " Na_2CO_3
= .0017 " NH_3

$\frac{N}{10}$ Na_2CO_3

1 c.c. = .0053 gram Na_2CO_3
= .00365 " HCl
= .0049 " H_2SO_4
= .0063 " HNO_3
= .0060 " $HC_2H_3O_2$

[illegible]

EXAMPLES OF VOLUMETRIC ANALYSIS.

21. Methods based on Neutralisation or Saturation. Alkalimetry; the determination of the strength of solutions of alkalies by titration with a standard solution of an acid.

A standard solution of an acid is added to a known quantity of the alkali under examination until the solution becomes neutral. This "end-point" is indicated by the change in colour imparted to certain vegetable colouring-matters added to the solution, which are extremely sensitive, yielding different tints according as the solution is alkaline or acid. From the number of c.c. of the acid used the amount of alkali present is found and the result given in *grams per litre*.

22. The indicators employed in alkalimetry and acidimetry are *litmus, phenolphthalein*, and *methyl-orange*. These react as under:

	With acids	*With alkalies*
Litmus	red	blue
Phenolphthalein	colourless	red
Methyl-orange	reddish pink	yellow

Litmus is affected by carbon dioxide and in the titration of a carbonate (which will evolve this gas) does not give a true indication of the end of the reaction until the carbon dioxide has been expelled by boiling.

Methyl-orange, on the other hand, is unaffected by carbon dioxide and is therefore specially useful for the titration of alkaline carbonates, no boiling being necessary. It, however, cannot be used in titrating organic acids.

Phenolphthalein is also affected by carbon dioxide but can be employed in the presence of organic acids. It cannot be used if ammonia is present.

23. Determination of the strength of a given solution of potassium hydrate by titration with $\frac{N}{10}$ H_2SO_4,(1) (2) using methyl-orange as indicator.

A known volume, say 10 c.c., is taken up with a pipette and placed in a beaker; water is added till there is about half-an-inch of liquid in the vessel together with a drop or two of methyl-orange. A burette is filled with $\frac{N}{10}$ H_2SO_4 and adjusted to the zero mark.(3) The beaker is placed on a sheet of white paper underneath the burette, which is clamped in a perpendicular position to its stand, and the acid run in very slowly, the contents of the beaker being stirred, or a circular motion imparted to them, until the change of colour of the methyl-orange from yellow to reddish pink indicates that the reaction(4) is completed. The number of c.c. of acid required is noted and the whole operation repeated once or twice until the end-point is accurately obtained. The strength of the solution of potassium hydrate is then calculated.

One example will illustrate how this is done; the method of calculation is equally applicable to subsequent volumetric experiments also. 10 c.c. of a solution of potassium hydrate, titrated with $\frac{N}{10}$ H_2SO_4, using methyl-orange as indicator, required (say) 30.1 c.c. of the acid for neutralisation.

10 c.c. of solution contain 30.1 × .0056 grams KHO.
1 litre contains 100 × 30.1 × .0056 grams KHO = 16.856 grams KHO.(5)

---

(1) It is evident that to accurately weigh out the necessary amount of sulphuric acid (actual H_2SO_4), or of potassium or sodium hydrate to make their solutions up to one litre is no easy matter as they are extremely hygroscopic and the weights taken would not be exact. Hydrochloric acid, being volatile, presents similar difficulties. Sodium carbonate can however, be obtained of great purity and, being neither [illegible] be weighed with perfect accuracy and a standard solution obtained. With this solution it is easy to determine how far short of being "standard" the comparatively roughly made solutions of the acids may be and more water or more acid can be added to bring them to the "standard." So, by means of an acid "standardised" in this way, [illegible] and water or the salt added until they, in turn, are standardised.

(2) [illegible] results are to be obtained. See remarks on indicators above.

(3) [illegible]

(4) [illegible]

(5) See [illegible] page.

24. Determination of the strength of a given solution of sodium carbonate by means of $\frac{N}{10}$ H_2SO_4, using methyl-orange as indicator.

10 or 20 c.c. of the sodium carbonate solution are transferred to a beaker, a drop or two of methyl orange added and, in a manner similar to that described in **23**, $\frac{N}{10}$ H_2SO_4 run in—a few c.c. at a time to begin with and then drop by drop as the reaction nears completion—till a permanent red colour is produced. The number of grams of sodium carbonate per litre are then calculated.

25. Determination of sodium carbonate, using litmus as indicator.

The process is carried out as described in the previous example but *the solution must be boiled to expel the carbonic acid gas* which acts on the litmus turning it red. The acid is added gradually until the colour changes from blue to a purple-red; the solution is then boiled until the blue colour returns, more acid run in and the boiling repeated until a single drop of acid causes a *permanent red* colour, unchanged by further boiling. The strength of the sodium carbonate is calculated as in former examples.

26. Determination of caustic alkali and carbonate when mixed.

When sulphuric acid is added to a mixture containing both hydrate and carbonate of an alkali the reaction takes place in two stages; first the hydrate and *half* the carbonate are neutralised according to the equations

$$2KHO + H_2SO_4 = K_2SO_4 + 2H_2O$$
$$\text{and } 2Na_2CO_3 + H_2SO_4 = 2NaHCO_3 + Na_2SO_4$$

half the carbonate becoming the bicarbonate. The bicarbonate is *not alkaline to phenolphthalein* so, if this indicator is added and such a mixture titrated with standard sulphuric acid, the phenolphthalein will become colourless when that stage in the neutralisation of the alkalies is reached represented by the expression,

$$\underbrace{2KHO + 2Na_2CO_3}_{\text{Mixture of hydrate and carbonate}} + 2H_2SO_4 = \underbrace{K_2SO_4}_{\text{Hydrate neutralised.}} + \underbrace{Na_2SO_4}_{\text{Half the carbonate neutralised}} + \underbrace{2NaHCO_3}_{\text{Half the carbonate changed to bicarbonate}} + 2H_2O$$

But the bicarbonate ($NaHCO_3$) yields a yellow colour with methyl-orange, which indicator is therefore added at this stage and the titration with acid continued till the liquid becomes pink, shewing the completion of the reaction, $2NaHCO_3 + H_2SO_4 = Na_2SO_4 + 2H_2O + 2CO_2$. The results are readily calculated from the amounts of acid used, (*a*) to decolourise the phenolphthalein, which will be that required to neutralise *all* the caustic alkali and *one half* the carbonate present, and (*b*) to complete the second stage of the reaction, which will be that required to neutralise *half* of the carbonate. This latter number, if doubled, gives the volume of acid necessary to neutralise *all* the carbonate. The sum of (*a*) and (*b*) is the acid required to neutralise *all* the alkali present.

A numerical example will illustrate how the results of these titrations can be calculated. To 20 c.c. of a solution containing sodium carbonate and potassium hydrate, phenolphthalein is added and $\frac{N}{10}$ sulphuric acid run in till the solution is colourless. 10 c.c. of acid are required. On the addition of methyl-orange and further titration, 5 c.c. are found to be necessary for complete neutralisation.

Acid required for neutralisation of the caustic alkali and *half* the carbonate ...... 10.00 c.c.
Acid required to complete the neutralisation, *i.e.*, to saturate *half* the carbonate . 5.00

Total acid required for both caustic and carbonate 15.00

Acid required for *all* the carbonate $2 \times 5 = 10$ c.c.
Acid required for the caustic $15 - 10 = 5$ c.c.

Hence 1 litre of solution contains

$$\text{Potassium hydrate} = \frac{1000 \times 5 \times .0056}{20} \text{ grams.}$$

$$\text{Sodium carbonate} = \frac{1000 \times 10 \times .0053}{20}$$

[illegible]

[illegible]

27. [illegible] procedure the strength of the following [illegible] expressing [illegible] grams per litre.

Potassium hydrate, using methyl-orange as indicator

Potassium hydrate, " phenolphthalein

Sodium carbonate, " methyl-orange

Sodium carbonate, " litmus

The proportions of caustic alkali and carbonate in the potassium hydrate, see **26**

Ammonium hydrate, using litmus or methyl-orange as indicator

28. Acidimetry; the determination of the strength of solutions of acids by titration with a standard solution of an alkali.

[illegible] *nitric acid* and *acetic acid*. [illegible] phenolphthalein.

29. The determination of ammonia by what is known as "titrating back"

should also be done. A normal solution of this substance would contain 17 grams NH_3 per litre but would lose its strength if left exposed to the air. A half normal solution is comparatively stable and a decinormal one keeps well. In determining free ammonia in this way a *known* amount of standard acid, *in excess of what will be required to neutralise the ammonia*, is added and [illegible] with standard alkali and methyl-orange as indicator.

From this the weight of NH_3 can be readily calculated. For example: to 10 c.c. of a solution of ammonia of unknown concentration are added 50 c.c. of $\frac{N}{10}$ sulphuric acid[1] and the *excess* of sulphuric acid titrated with $\frac{N}{10}$ potassium hydrate (using methyl-orange as indicator) of which 20 c.c. are required to neutralise the excess of $\frac{N}{10}$ H_2SO_4 ∴ 50 − 20 = 30 c.c. is the amount of $\frac{N}{10}$ H_2SO_4 required to neutralise the sample of ammonia.

As each c.c. of $\frac{N}{10}$ H_2SO_4 is equivalent to .0017 gram of NH_3

∴ 1 litre of the ammonia solution contains

$$\frac{1000 \times 30 \times .0017}{10} \text{ grams ammonia}$$

Standard acids and alkalies can be used for a number of [illegible].

---

[1] As the ordinary burette is seldom graduated for use with more than [illegible] a pipette to remove an aliquot portion for each titration. For example, if the [illegible] pipetted out into a beaker and titrated. It is a simple matter to [illegible] of the original solution are made up to 500 [illegible]

[illegible]

[illegible] number of c.c. of acid equivalent to the amount of alkali added [illegible]

30. *To estimate a carbonate, insoluble in water, by dissolving it in an excess of standard acid and titrating back.*

2 grams of a sample of "precipitated chalk" are weighed on a watch-glass and transferred to a beaker, carefully washing the [illegible] powder and adding from 50 to 100 c.c. of water. Into the water containing the carbonate in suspension is run *an excess* of normal HCl till all effervescence ceases and the amount used noted. Two or three drops of methyl-orange are added and the excess of acid titrated with normal KHO. If the amount of normal HCl added in the process of solution is 60 c.c. and 20.5 c.c. normal KHO are required to neutralise the *excess* of acid,

60 − 20.5 = 39.5 c.c. is the amount of normal HCl that reacted with the sample of chalk.

As 1 c.c. normal HCl is equivalent to .05 gram $CaCO_3$[1]

the sample contains 39.5 × .05 = 1.975 grams $CaCO_3$.

31. *Determination of the "temporary hardness" of water by titration with standard acid.*

Temporary hardness in water is due to the presence in small quantities of carbonates of calcium (or magnesium) rendered soluble by carbon dioxide. The amount is usually so little that if normal or even decinormal acid were used to decompose them the error would be very great owing to the small quantities required for the titration. A much less concentrated acid is employed, therefore, $\frac{N}{50}$ being a suitable strength. This can be prepared by the student by taking 20 c.c. of the normal hydrochloric acid used in the previous exercise and making that volume up to 1000 c.c. with water. The determination may then be done in two ways:

(a) To 100 c.c. of the "hard" water under examination are added two or three drops of methyl-orange and $\frac{N}{50}$ HCl run in till the end-point is indicated by the solution turning red.

(b) In a manner similar to **30** an *excess* of acid may be added and the excess estimated by $\frac{N}{50}$ KHO, which can be prepared from the normal KHO in the same way as the $\frac{N}{50}$ HCl is made from the normal acid.

From the amount of acid required to react with the carbonate the "degree of hardness" can be calculated, a degree of hardness being taken as 1 part $CaCO_3$ per 100,000 of water. Each c.c. of $\frac{N}{50}$ HCl is equivalent to .001 gram $CaCO_3$. So, if the sample required 20 c.c. $\frac{N}{50}$ HCl to decompose the $CaCO_3$ then the 100 c.c. sample will contain 20 × .001 gram $CaCO_3$ = .02 gram $CaCO_3$

100,000 parts will contain 1000 × .02 = 20 grams $CaCO_3$.

This water would be said to have a hardness of 20 degrees.

32. *Methods based on Oxidation.*

Quite a number of oxidising agents are employed in the form of standard solutions for determining the amounts of substances that are capable of being oxidised quantitatively. One of the most useful solutions of this kind is potassium permanganate, which has the additional advantage of *requiring no indicator other than itself.* In the process of oxidising it becomes *reduced* to a salt of manganese which is practically colourless and the slightest trace of any permanganate over and above what is required to complete the reaction imparts a pink tinge to the solution. It is used for estimating iron, and for oxalic acid and oxalates; indirectly it can be used for the determination of any base capable of yielding an insoluble oxalate.

33. For making a normal solution of permanganate only one-fifth of the molecular weight in grams is taken in a litre of water. The definition of a normal solution previously given states that a litre of such a solution is to contain the *chemical equivalent* of 1 gram of hydrogen. In permanganate the oxygen is the *active* constituent so such a quantity of the salt is used as will contain 8 grams of *oxygen available for oxidising purposes,* 8 grams of oxygen being equivalent to 1 gram of hydrogen. If the formula of the permanganate—doubled to allow of what follows being expressed—be divided

---

[illegible]

[1] [illegible] from the equation $CaCO_3 + 2HCl = CaCl_2 + H_2O + CO_2$ [illegible]

[illegible]

up to represent the oxides [illegible] which it might be resolved in process of performing its oxidising function it can be written thus, $\underset{94}{K_2O}$, $\underset{142}{2MnO}$, and $\underset{80}{O_5}$. Oxidation with permanganate in volumetric analysis requires the presence of (preferably) free sulphuric acid [illegible] the decomposition products of the salt forming with it potassium sulphate and manganese sulphate [illegible] otherwise the oxide of the latter was precipitated, while the proportion of oxygen which is set free oxidises whatever oxidisable body it may be in contact with, thus,

$$\underset{2 \times 158}{2KMnO_4} + 3H_2SO_4 = K_2SO_4 + MnSO_4 + 3H_2O + \underset{80}{O_5}$$

There are thus 80 grams of available oxygen in 316 of permanganate, or 40 in the formula-weight KMnO$_4$ (158). How many grams of this salt, then, will it be necessary to have contained in one litre in order to obtain a normal solution? If there are forty grams of available oxygen in 158 grams of permanganate $\frac{158 \times 8}{40}$ = 31.6 grams will contain the necessary 8 grams of available oxygen. normal permanganate, therefore, contains 31.6 grams of the salt per litre and a decinormal solution will contain 3.16 grams. Before use this solution will have to be accurately standardised, just as the normal sulphuric acid was standardised against pure sodium carbonate. In the case of permanganate solution this is done with pure iron wire or with pure crystallised oxalic acid. The method of procedure is the same as in the following exercises, in which examples it will be presumed that the standard permanganate employed is exactly normal or decinormal, or such fraction of normal as it is stated to be

34. Standard permanganate has its principal application in determining iron, by its power of converting ferrous salts into ferric salts; and in determining free oxalic acid which is broken up by it into water and carbon dioxide. The nature of these reactions can best be seen thus

$$(a)\ 2KMnO_4 + \underset{(10FeO \cdot SO_3)}{10FeSO_4} + 8H_2SO_4 = K_2SO_4 + 2MnSO_4 + \underset{(5Fe_2O_3 \cdot 3SO_3)}{5Fe_23SO_4} + 8H_2O$$

or, expressing oxidation only, $10FeO + O_5 = 5Fe_2O_3$; that is to say, 560 grams of iron are oxidised by 80 grams of oxygen.

$$(b)\ 2KMnO_4 + \underset{(oxalic\ acid)}{5H_2C_2O_4} + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 8H_2O + 10CO_2$$

or, expressing oxidation only, $5H_2C_2O_4 + O_5 = 5H_2O + 10CO_2$; that is, 450 grams oxalic acid are oxidised by 80 grams of oxygen. Thus 8 grams of oxygen are equivalent to 56 grams of iron and to 45 grams of anhydrous oxalic acid. As a decinormal solution of permanganate contains .8 gram available oxygen per litre (see ante), each c.c. of it will be the measure of .0056 gram Fe and of .0045 gram $H_2C_2O_4$ [illegible]

35. *Determination of iron in a solution of ferrous sulphate or other ferrous salt.*

A measured quantity of the ferrous solution is transferred to a flask or beaker, and diluted somewhat with distilled water,[13] about half its volume of dilute sulphuric acid added and $\frac{N}{10}$ KMnO$_4$ run in, the contents of the beaker being thoroughly mixed. The titration is continued until the solution of permanganate produces a faint permanent pink best seen if the containing vessel is placed on a white tile or sheet of paper. Knowing that each c.c. of $\frac{N}{10}$ KMnO$_4$ is equivalent to .0056 gram of iron, the quantity of ferrous salt present—*whatever salt it may be*[14]—can readily be calculated; for every 56 grams of iron can yield 56 + 32 + 64 = 152 grams FeSO$_4$[15] or 278 grams of FeSO$_4$7H$_2$O, the crystallised salt. So for any other ferrous salt

An example will illustrate the simplest method of making such a calculation:—10 c.c. of a solution of ferrous sulphate required 24.8 c.c. of $\frac{N}{10}$ KMnO$_4$ for oxidation

∴ 10 c.c. of solution contains 24.8 × .0056 gram Fe = .1388 gram Fe

and $\underset{56}{Fe} : \underset{152}{FeSO_4}$ = amount of Fe found : amount of FeSO$_4$ to which that quantity of Fe is equivalent

this amount of FeSO$_4$ = $\frac{.1388 \times 152}{56}$ = .3767 gram in 10 c.c.

= 37.67 grams per litre

[illegible] titrations with permanganate the solution must be acidified with sulphuric acid. Nitric acid should not be present and hydrochloric [illegible] to become oxidised by the permanganate and to evolve chlorine. Organic matter must not be present [illegible] acid is $H_2C_2O_4 \cdot 2H_2O$ [illegible] .0063 gram.

Ferrous salts rapidly oxidise in solution especially if the water has not been freshly [illegible] *perfectly* [illegible]

[illegible] The term "oxidation" is applied [illegible] oxygen in their composition. When ferrous chloride (Fe"Cl$_2$), becomes ferric chloride (FeCl$_3$) it is said to have been oxidised [illegible] used to express the change that takes place in a substance analogous to the conversion of a lower into a higher oxide

[illegible] Fe 56 S 32 O 16 K [illegible] Mn [illegible]

36. Determination of iron in ferric sulphate or other ferric salt.

[illegible] what has been said it will be seen that permanganate only affects iron salts when they are in the *ferrous* condition: this, however, does not prevent its use for estimating *ferric* salts also, for these can be *reduced* to ferrous salts, the iron then determined by oxidation with standard permanganate as in the previous example, and the amount thus found "calculated to" the particular ferric salt.

[illegible] the amount of say iron-alum ($KFe2SO_4 12H_2O$) in a solution of that salt, [illegible] 20 c.c. [illegible] a beaker or an Erlenmeyer flask, add water and about 10 c.c. of concentrated [illegible]. A few fragments of metallic zinc are added and the flask set aside till the evolution of hydrogen ceases and the zinc is all dissolved. The solution may require to be heated to effect the complete [illegible] the hydrogen at the moment of its liberation reacts with the ferric sulphate [illegible]. This reduction must be complete and to test if this is so a drop [illegible] of a glass rod placed on a white surface, such as the lid of a porcelain [illegible] are added. If any ferric salt remains a red colour will be produced and further reduction with zinc and acid must be resorted to. When free from ferric salt, that is, when [illegible] colour with sulphocyanate, the flask is cooled under the tap and at once titrated with [illegible]

The amount of ferric salt is then calculated as follows. Let 20 c.c. be the volume of solution taken for the determination and after reduction with zinc and sulphuric acid 45 c.c. $\frac{N}{10}$ $KMnO_4$ are found necessary to oxidise it. Then 20 c.c. of sample will contain 45 × .0056 gram Fe = .252 gram Fe.

To calculate this to [illegible]:

$$Fe : KFe2SO_4 12H_2O :: \text{amount of Fe found} : \text{grams } KFe2SO_4 12H_2O$$

amount of $KFe2SO_4 12H_2O$ in 20 c.c. = [illegible] grams

Hence, a litre contains [illegible] grams.

37. Determination of ferrous and ferric salts when mixed.

[illegible] known volume) is reduced by means of zinc and sulphuric acid [illegible] 36 [illegible] *ferrous salt*. In another portion of equal volume [illegible] of the solution the ferrous [illegible] determined as described in 35.

Let [illegible] mixture be one of ferrous sulphate and ferric sulphate, then the calculation of the composition of the solution is made as follows:

[illegible] is obtained the total iron

[illegible] obtained that present as ferrous salt

[illegible] Fe in [illegible] Fe which is present as ferric salt

[illegible] then calculated to $FeSO_4$ and to Fe_23SO_4 respectively by the arithmetical process described in former examples.

38. Determination of the strength of a solution of permanganate by iron wire.

About [illegible] gram of pure iron wire is weighed carefully, transferred to an Erlenmeyer flask and about 100 c.c. [illegible] added. The flask and contents are placed on a sand-bath and allowed to simmer [illegible]: a few minute particles of carbon often remain but these will not [illegible]. [illegible] may, with advantage, be inserted in the neck of the [illegible] while not interfering with the escape of the hydrogen. The flask [illegible] water added if need be, and the ferrous sulphate solution titrated at once with the permanganate solution whose strength is wanted. The calculation can be done as follows:

[illegible] grams Fe it must also be equivalent to [illegible] gram of $KFe2SO_4 12H_2O$ [illegible]

[illegible]

If .2 gram of iron is found to require 50 c.c. $KMnO_4$ for oxidation, and it is known by what has been explained earlier that 31.6 grams $KMnO_4$ can oxidise 56 grams of iron, then the amount of $KMnO_4$ that can oxidise .2 gram must be $\frac{31.6 \times .2}{56}$, *i.e.* $\frac{31.6}{280}$ gram, the amount in [illegible]

1 litre of the permanganate will contain $\frac{31.6 \times 1000}{280 \times 50}$, *i.e.* 2.26 grams.

As 31.6 grams permanganate per litre constitutes a normal solution, the strength of the one under examination must be $\frac{2.26}{31.6}$ of normal, namely $\frac{N}{14}$ approximately.

Another method of reasoning, which leads to the same result, is :- 50 c.c. of the unknown permanganate are found to oxidise .2 gram of iron ; and it is known that, as each c.c. of normal permanganate is equivalent to .056 gram of iron, 50 c.c. of such a solution must be capable of oxidising 50 × .056, namely 2.8 gram of iron ; therefore the solution must be $\frac{.2}{2.8}$ of normal, $\frac{N}{14}$.

39. Determination of oxalic acid by titration with standard permanganate.

From what has been said in **34** it will be seen that oxalic acid is readily converted into carbon dioxide and water by solutions of permanganate.

To perform this estimation the oxalic acid solution is acidified with sulphuric acid, *gently heated* to a temperature of about 60° C.* and the permanganate run cautiously in from a burette. An appreciable time is necessary for the oxidation of the oxalic acid and consequent reduction of the permanganate so the pink colour does not disappear as rapidly as in the titration of ferrous salts. Especially is this the case towards the end of the reaction, and great care must be exercised at this stage, the permanganate being added cautiously and the solution allowed to stand to permit of the colour being discharged otherwise the end point may be overstepped. At the first sign of a *permanent* pink after the solution has stood for a minute or so the titration may be considered finished and one or two more titrations should be done till the student is satisfied that he has hit off the end-point exactly. Each c.c. of $\frac{N}{10}$ $KMnO_4$ oxidises .0045 gram anhydrous $H_2C_2O_4$ (14). The amount of oxalic acid present can easily be calculated.

40. Determination of a soluble oxalate

On the addition of sulphuric acid to a soluble oxalate, oxalic acid is set free : the above estimation can therefore be done in the same way as described in **39**, the amount of oxalic acid found being calculated to the particular oxalate employed.

41. Determination of metals that yield insoluble oxalates.

Taking calcium as an example of a metal yielding an insoluble oxalate, the metal is completely precipitated as oxalate, the precipitate washed free from all soluble matter, redissolved in acid and the liberated oxalic acid titrated with standard permanganate. From the numerical relation between $H_2C_2O_4$, the calcium oxalate CaC_2O_4 and the actual salt of calcium employed, the desired result can be calculated.

To perform the estimation, a known quantity of a soluble calcium salt is taken, diluted with water, ammonia added till the solution smells strongly of that reagent and the liquid heated to boiling. A warm solution of ammonium oxalate is then added, the mixture boiled for a few minutes and the precipitated calcium oxalate allowed to settle. The supernatant liquid is decanted through a filter, the precipitate washed once or twice by decantation and transferred to the filter where it is washed with hot water till the filtrate gives no reaction when tested for oxalic acid. The precipitate is best transferred to the flask in which the titration is to be performed by placing the funnel in the mouth of the flask, puncturing the apex of the filter and washing it through with a fine jet of water from a wash-bottle. Any precipitate that remains adhering to the paper is dissolved off with *a little* hot hydrochloric acid, followed by more washing down with hot water. In this way every trace of calcium salt is transferred to the flask. Any precipitate in the flask that has not been dissolved by the acid which was poured on the filter is now treated with the *minimum amount of hydrochloric acid that will effect its solution* and no more.(20) Sulphuric acid is now added, the mixture heated to about 60° C. and, *without further delay*, titrated with standard permanganate. The number of c.c. of permanganate required gives the amount of oxalic acid that went to form the insoluble CaC_2O_4, from which the calcium is calculated.

---

* It is possible to insert the hand into water at 60° but not to retain it there with any degree of comfort. The temperature required for the experiment can therefore be approximately guaged when the beaker or flask containing the solution can be grasped firmly in the hand and held for a space of about two seconds only.

(14) See note 14.

(20) As each c.c. of $\frac{N}{10}$ $KMnO_4$ is equivalent to only .0045 gram $H_2C_2O_4$ (and consequently to .0064 gram CaC_2O_4) it was [illegible] satisfactory at this stage to dilute the solution obtained as above to a known volume and remove an aliquot portion for titration with the permanganate in the presence of sulphuric acid. See also note *.

42. [illegible] standard [illegible] to the determination of the strength of certain of the laboratory reagents. For example (*a*) The amount of ferrous sulphate in the laboratory solution of that salt. (*b*) The [illegible] (*c*) The amount of calcium chloride in the laboratory solution. (*d*) The strength of the oxalic acid.

43. Decinormal potassium bichromate.

Standard solutions of potassium bichromate are frequently employed in place of permanganate [illegible] they cannot be used [illegible]. Titrations with bichromate can be done in the presence of hydrochloric acid, which acid is unsuitable [illegible]. Estimations done with bichromate require an *outside indicator*, the one used being a *freshly prepared* solution of potassium ferricyanide which yields a blue colour [illegible] absence of the blue colour, when a drop of the [illegible] placed on a [illegible] [illegible]

[illegible] potassium bichromate and a ferrous salt can be expressed thus:

$$[illegible]\ K_2Cr_2O_7\ [illegible]\ 3Fe_2\ 3SO_4 + K_2SO_4 + Cr_2 3SO_4 + 7H_2O$$

[illegible]

The action of the *oxygen* on the ferrous salt can also be represented in this way:

$$[illegible]FeSO_4 + 3H_2SO_4 + O_3 = 3Fe_2\ 3SO_4 + 3H_2O$$

[illegible]

In order to ascertain how much bichromate is required to make a litre of a normal solution, an argument similar to that employed under normal permanganate will suffice. If the formula of potassium bichromate is dissected it may be written K_2O, 94; Cr_2O_3, 152; and O_3, 48; molecular weight, 294. Therefore, as 294 grams bichromate contain 48 grams of *available* oxygen, the weight of bichromate necessary to yield a normal solution [illegible] when contained in a litre of water will be [illegible] grams. A decinormal solution, consequently, contains 4·9 grams $K_2Cr_2O_7$ per litre, and each c.c. will oxidise .0056 gram of iron in combination as a ferrous salt to the ferric condition. Such a standard solution may be conveniently labelled "$\frac{N}{10}$ $K_2Cr_2O_7$, 1 c.c. = .0056 gram Fe."

44. Determination of ferrous sulphate by decinormal potassium bichromate.

The general directions given in **35** are followed, with this difference that in titrations with bichromate [illegible]. For this purpose a *fresh* solution of potassium ferricyanide is made by dissolving [illegible] number of drops of this are spotted [illegible] basin. From time to time a drop [illegible] indicator touched with it. As long as any blue colour is produced the oxidation is incomplete and the addition of bichromate is continued till a drop of the solution no longer causes any change in the ferricyanide. The reaction is now complete, all the ferrous salt having been [illegible] ferric salt. From the amount of original substance taken for analysis and the number of c.c. of N/10 bichromate used the quantity of ferrous sulphate can be calculated.

The first few titrations with bichromate will, of necessity, be inaccurate owing to the removal [illegible] salt during the "spotting" process. The best method of procedure is to rather overstep [illegible] learning in this way the number of c.c. that may safely be added at once and [illegible] take any out with the glass rod. The last few drops can [illegible]

45. Determination of the strength of the laboratory ferric chloride solution by standard bichromate.

[illegible] **44**, after the [illegible] **35**.

[illegible]

46. Determination of ferrous and ferric salts in a mixture by standard bichromate.

Th[illegible] described [illegible] **37** [illegible] **44** [illegible] be used for reducing the ferric salt [illegible] works best though it is slower and introduces a salt of zinc into the solution which is apt to interfere with the action of the ferricyanide indicator. [illegible] carried out as in **36**.

If the latter method is employed sufficient stannous chloride must be added to complete the reaction $Fe_2Cl_6 + SnCl_2 = 2FeCl_2 + SnCl_4$, but the end-point of the reduction cannot be tested for by potassium ferricyanide as in **36**, so the addition of a *slight excess* of stannous salt is unavoidable. The excess [illegible] afterwards be removed by precipitation with mercuric chloride or it will react with the bichromate. [illegible] prepare the solution for titration, acidify with concentrated hydrochloric acid, heat to boiling [illegible] of the laboratory stannous chloride, boil and add more reagent little by little, gently [illegible] time, till the solution is colourless; this may take some time. When this point is reached pour in *quickly* a larger quantity of mercuric chloride solution than it is thought will be required to precipitate the excess of [illegible] a white precipitate of mercurous chloride will form which will not interfere with the subsequent titration with bichromate. The reaction [illegible] $2HgCl_2$ [illegible] $SnCl_4 + 2HgCl$, but if sufficient mercuric chloride is not added *at once* then the reaction [illegible] $SnCl_4 + 2Hg$ will occur and the precipitate will be gray or black. If this takes place there is no remedy but to repeat the analysis from the beginning. The results of the experiment are calculated as in **37**.

47. Determination of the strength of a solution of potassium bichromate by means of iron wire.

Apply the principles contained in **38, 43** and **44**, and from the results obtained calculate what is the strength of the potassium bichromate in terms of normal.

48. Standard iodine solution and its uses.

Iodine in the presence of water is capable of oxidising a number of substances quantitatively the iodine becoming hydriodic acid (or an iodide). As the smallest trace of *free* iodine imparts a [illegible] to solutions of starch the end-point of the reaction can be clearly obtained[1]. Estimations are done *directly* with standard solutions of iodine or *indirectly* by determining the amount of *free* iodine that the body liberates from combination. Free iodine is capable of very accurate determination by means of sodium thiosulphate, and these two reagents in conjunction find numerous applications in analytical work.

49. Decinormal iodine.

12.7 grams of pure iodine are weighed out [illegible] and transferred to a litre flask. Water is poured in and about 20 grams of pure potassium iodide added. [illegible] mixed thoroughly till solution is complete and [illegible] flask filled up to the litre mark. This solution, if correct, will contain .0127 *gram iodine* [illegible]

50. Decinormal sodium thiosulphate.

The quantity of *anhydrous* sodium thiosulphate required for a litre of a normal solution will be seen from the equation expressing the reaction between this salt and free iodine

$$2Na_2S_2O_3 + I_2 = 2NaI + Na_2S_4O_6$$

Thus, a normal solution of thiosulphate contains [illegible] grams per litre, a decinormal one [illegible]. *Each c.c. will be equivalent to .0127 gram iodine.*

51. Determination of iodine by titration with $\frac{N}{10}$ thiosulphate.

A known volume of a solution of iodine is placed in a beaker—resting on a white surface—and diluted to a convenient bulk with water. Standard thiosulphate is run in slowly, the solution being kept well mixed, until the colour of the iodine *almost* disappears. A few drops of starch[2] solution are now added causing a blue colour, and the thiosulphate added drop by drop till the complete discharge of the blue colour indicates that the reaction is at an end. The quantity of iodine in the sample is readily calculated. The converse of this should be done by the student, namely, delivering the standard iodine solution from a burette into a solution of thiosulphate containing a few drops of clear starch solution. The appearance of a permanent blue colour indicates the presence of the smallest excess of iodine.

---

[1] This blue coloured substance is usually known as iodide of starch; recent researches, however, point to it not being a chemical compound but a solid solution of iodine in starch. [illegible]

Iodine is sparingly soluble in water but readily [illegible] of iodine.

Crystallised sodium thiosulphate is $Na_2S_2O_3 5H_2O$, having a molecular weight of 248. In making the solution, therefore, 24.8 grams [illegible] taken. [illegible] that 1 litre of a normal solution of the salt [illegible] that this amount is the chemical equivalent of 127 grams of [illegible]

[2] Starch solution does not keep well and should always be freshly prepared. This is best done by [illegible] a few grams of white starch [illegible] mortar to form a milky paste, pouring this into a comparatively large amount of *boiling* water and then adding about twice [illegible] the mixture. The solution is allowed to settle and the clear liquid poured off for use.

52. Determination by direct titration with standard iodine.

[illegible] de, of sulphur dioxide, of arsenious salts and of antimonious salts [illegible]

[illegible]

[illegible] H_2O [illegible]

[illegible] H_2O [illegible]

[illegible] $2HI + H_2SO_4$

[illegible]

53. Determination of hydrogen sulphide in aqueous solution by standard iodine.

When solutions of hydrogen sulphide are *sufficiently dilute* [illegible] the hydrogen sulphide and iodine takes place according to the equation above, but if the solutions contain more than .04 per cent *by weight* the change may not take place exactly as represented and therefore the method is useless. A sufficiently weak solution of the hydrogen sulphide can, however, be readily prepared by making up a definite volume of the hydrogen sulphide water to a known volume with air-free water. Even at best the method of analysis is not free from error [illegible] of the H_2S gas into the air and by oxidation.

[illegible] added as indicator and the standard iodine solution run in. From the amount used before the permanent blue tinge is produced [illegible]

A more accurate method is to add to a known volume of the standard iodine a measured [illegible]

54. Determination of arsenic by standard iodine.

The [illegible] given in **52** shews how iodine and [illegible]

55. Determination of antimony in "Tartar-emetic" by standard iodine.

[illegible] **52** represents the reaction that takes places between antimony oxide (and [illegible] $NaHCO_3$ added before titration.

56. Determination of sulphur dioxide in aqueous solution by standard iodine.

[illegible] in precisely the same manner as hydrogen sulphide [illegible] A more accurate method is described further on, **60**

[illegible] **52**

57. Determination of tin.

Iodine and stannous chloride react in solution thus, $SnCl_2 + I_2 = SnCl_2I_2$, *two* atoms of iodine being therefore [illegible] or equivalent to *one* atom of tin. If metallic tin is given for analysis it must first be dissolved in hydrochloric acid, some $KNaC_4H_4O_6$ (Rochelle-salt) added and then sodium bicarbonate in excess before titration with standard iodine and starch.

58. Determination by titrating the excess of iodine added with standard sodium thiosulphate.

Both hydrogen sulphide and sulphur dioxide can be more accurately determined by adding a known volume of the [illegible] standard iodine solution [illegible] of known volume and ascertaining the amount of iodine not used up in the reactions by titration with standard thiosulphate as described in **51**.

59. Determination of chlorine in chlorine-water by iodine and thiosulphate.

To a known volume of *dilute* chlorine water is added [illegible] excess of potassium iodide; the solution is thoroughly mixed and the liberated iodine determined by starch and thiosulphate. [illegible] liberate 127 grams of iodine from the potassium iodide; from this the chlorine can be calculated.

60. Determination of sulphur dioxide in a sulphite by iodine and thiosulphate.

To a known volume of the sulphite solution is added an excess of standard iodine—also of known volume. The excess of iodine is titrated with starch and thiosulphate and the difference between the amount so [illegible] and the total iodine added is the proportion of iodine that has taken part in the reaction:

$$Na_2SO_3 + I_2 + H_2O = 2HI + Na_2SO_4.$$

127 grams of iodine are here equivalent to 32 grams SO_2, to 63 grams Na_2SO_3 or to 126 grams $Na_2SO_3.7H_2O$.

61. Determination of copper indirectly.

When potassium iodide is added to a solution of copper sulphate the following reaction takes place.

$$2CuSO_4 + 4KI = Cu_2I_2 + I_2 + 2K_2SO_4$$

Every 63 parts of copper (or 159 parts of anhydrous copper sulphate) are equivalent to 127 parts of iodine.

The copper solution must not contain any free mineral acid. To ensure this being the case sodium carbonate is added to the solution until a faint permanent precipitate forms; acetic acid is then added carefully till the copper precipitate just dissolves. The free iodine is titrated with standard thiosulphate and starch and the copper calculated.

62. Methods based on precipitation.

In explaining the principles of volumetric analysis (**3** and **4**) the precipitation of silver chloride by the interaction of solutions of sodium chloride and silver nitrate was used as an illustration. Standard solutions of the latter salt can therefore be employed to determine the amount of halogen in any soluble chloride, provided an accurate way of determining the "end-point" is known. The reaction,

$$\underset{\substack{23+35.5 \\ 58.5}}{NaCl} + \underset{\substack{108+14+48 \\ 170}}{AgNO_3} = \mathbf{AgCl} + NaNO_3,$$

indicates that 170 grams silver nitrate are equivalent to 35.5 grams chlorine, 58.5 grams common salt, and so on for any other chloride that permits of this method being used. The completion or end-point of the reaction can be seen by agitating the precipitated silver chloride until it coagulates, and consequently settles, and then ascertaining whether or not an additional drop of either reagent will yield a milkiness or opalescence. But this method requires special precautions—one might almost say special apparatus—and in *neutral* solutions of chlorides it is easier to take advantage of the fact that when silver nitrate is added to a mixture containing a chloride and a small quantity of a chromate, *all the chlorine will be precipitated as* **AgCl** *before the chromate of silver* ($\mathbf{Ag_2CrO_4}$) *forms*. Chromate of silver has a chocolate-red colour and hence the first trace of an excess of silver salt, above that which is necessary to convert all the chlorine in the solution into white silver chloride will be rendered apparent by the appearance of the permanent [illegible] tinge that silver chromate imparts to the solution and suspended silver chloride. Silver chromate only serves as an indicator in *neutral* solutions, free acid preventing its formation. As chlorides in potable waters are estimated in this way solutions of fiftieth-normal and even hundredth-normal silver nitrate are often employed.

63. Determination of chlorine in a dilute solution of common salt.

[illegible] potassium chromate (K_2CrO_4) are added to a definite volume of the salt solution [illegible] $\frac{N}{10}$ [illegible] $\frac{N}{10}$ $AgNO_3$ is equivalent to [illegible] is obtained.

In a similar manner the student should determine the strength of the [illegible] chloride and of the calcium chloride ($CaCl_2$).

64. Indirect estimations by means of standard silver nitrate.

As the completion of the reaction between silver nitrate and a soluble chloride is readily observed through the use of the chromate indicator it is evident that all compounds capable of being converted into neutral chlorides by evaporation to dryness with hydrochloric acid can be accurately determined in this way. The ***alkalies, alkaline-earths*** and many other bases can thus be estimated, as also ***chlorates*** and ***nitrates.*** The chlorine only is determined and the result calculated to the particular salt under examination. ***Chlorates*** are converted into chlorides by ignition and the chlorine then determined. ***Nitrates*** are evaporated on the water-bath with concentrated hydrochloric acid once or twice till the nitric acid is all expelled, heated in an air-bath [illegible] dissolved and titrated with standard silver solution.

65. Determination of sodium and potassium chlorides when mixed.

The total weight of the mixed chlorides of potassium and sodium is obtained by weighing, and the chlorine estimated by standard silver nitrate. If S represent the weight in grams of the sodium chloride and potassium chloride mixed, and C the weight in grams of the total chlorine found, then X, the number of grams of sodium chloride in the mixed chlorides, is found from the formula,

$$X = \left(2.1032 \times C - S\right) \times 3.6[illegible]$$

The amount of potassium chloride will be S − X grams.

[illegible]

$$\frac{Cl}{NaCl}X + \frac{Cl}{KCl}(S - X) = C$$

$$X\left(\frac{Cl}{NaCl} - \frac{Cl}{KCl}\right) = C - \frac{S\,Cl}{KCl}$$

[illegible] $\frac{KCl}{Cl}$ [illegible]

$$X\left(\frac{KCl}{NaCl} - 1\right) = \frac{KCl}{Cl}C - S$$

$$X = \left(\frac{KCl}{Cl}C - S\right)\left(\frac{NaCl}{KCl - NaCl}\right)$$

[illegible]

66. Determination of the "available chlorine" in bleaching-powder.

Bleaching-powder is a compound of uncertain composition containing the chloride, hypochlorite and probably the hydrate of calcium, sometimes even the chlorate: if composed of the first two its composition would be $CaCl_2\,Ca(ClO)_2$; more often half this formula is taken, namely $CaOCl_2$, the "chloro-hypochlorite" of calcium. Were bleaching powder entirely $CaOCl_2$ then all the chlorine would be "available" for bleaching or oxidising purposes[31]; but so many changes take place in its composition that in place of having 55% of its weight of chlorine available, as the formula $CaOCl_2$ would indicate, it seldom has more than 35% and sometimes as little as 20%. In valuing bleaching powder the object is to ascertain how much chlorine *capable of liberating oxygen from water* the sample contains. This is done in several ways, one of them being to determine its oxidising power on a solution of arsenious oxide, a reaction expressed by the equation,

$$As_2O_3 + 2CaOCl_2 = As_2O_5 + 2CaCl_2$$
$$198 \qquad 4 \times 35.5$$

Thus, 198 grams of arsenious oxide are equivalent to 4 × 35.5 grams of chlorine, and consequently to 2 × 16 grams of oxygen. Therefore $\frac{198}{4}$ grams arsenious oxide are equivalent to 35.5 grams chlorine and to 8 grams oxygen. A decinormal solution of this must contain $\frac{198}{40}$ grams, and each c.c. will be equivalent to .0035 gram Cl. The amount of chlorine found as the result of titrating a sample of bleaching-powder with arsenious oxide is known as the "available chlorine."

The indicator used to determine the end-point of the reaction is commonly called "starch paper," but is more properly "starch-iodide-paper," for it consists of strips of bibulous paper that have been dipped in a mixture of starch solution and potassium iodide—about one part of starch and of the iodide to a hundred parts of water—and allowed to dry. Any substance capable of liberating iodine from potassium iodide will cause this starch-paper to turn blue and the presence of any unacted-on bleaching-powder in the solution being examined will at once be observed if a drop of it is brought in contact with the test-paper. The titration is done as follows

67. A known volume of the bleaching-powder solution[32] is placed in a flask, diluted somewhat with water and the standard solution of arsenic[33] run into it from a burette. From time to time a drop of the solution is removed on the end of a glass stirring-rod and brought into contact with a strip of the starch-paper. As soon as no coloration is produced on the paper the reaction is complete and the volume of arsenic solution is noted. Two more determinations should be done in a similar manner to ensure an accurate result, for the frequent removal of drops in the process of "spotting" the starch-paper will of necessity lessen, though slightly, the total volume of solution subjected to the action of the arsenic solution.[34] From the quantity of arsenic solution required the amount of "available chlorine" per litre of the bleaching-powder solution is calculated.

68. Determination of "available chlorine" by iodine and thiosulphate.

If hydrochloric acid be added to a solution of bleaching powder *containing some potassium iodide*, the chlorine liberated by the action of the acid on the bleaching compound will in turn liberate an equivalent amount of iodine from the potassium iodide. This quantity is readily determined by titration with sodium thiosulphate and starch, **51**. 127 grams of iodine being equivalent to 35.5 grams of chlorine, the "available chlorine" in the sample is easily found

Take 20 c.c., or any other known volume, of the solution of bleaching-powder (note 32), add an excess of potassium iodide solution and enough dilute hydrochloric acid to render the liquid decidedly acid. Then titrate the liberated iodine with starch and thiosulphate and from this calculate the amount of available chlorine.

---

[31] That is, for liberating nascent oxygen from water, the oxidising power of chlorine being dependent on the presence of water $Cl_2 + H_2O = 2HCl + O$. This would also be the amount of chlorine available for "chlorinating" purposes.

[32] Bleaching-powder, as will be readily seen from what has been said regarding its composition, is not completely soluble in water. A solution of it is best prepared by triturating a weighed sample with water in a mortar, allowing it to settle and pouring the clear liquid into a litre flask. This process is repeated once or twice and the whole of the powder, whether in solution or not, finally washed into the flask, which is then filled up to the mark. Before the withdrawal of a sample for analysis the flask and contents must be shaken. The solution which is always slightly milky deteriorates rapidly.

[33] To prepare a decinormal solution of arsenious oxide $\frac{198}{40}$, i.e. 4.95 grams of the pure resublimed oxide are placed in a litre flask with about 250 c.c. of distilled water and about 20 grams of pure sodium carbonate. After heating on a water-bath and shaking [illegible] the contents made up to a litre.

[34] See last paragraph **44**.

69. Determination of nitrogen.

Perhaps the most rapid, simple and at the same time accurate method for determining nitrogen is that first proposed by Kjeldahl and which bears his name. Other chemists (notably Gunning, Wilfarth and Jodlbauer) have improved on the original method and made it applicable to the determination of nitrogen in innumerable organic and inorganic compounds. Coal, grain, fertilisers, nitrates, ferro- and ferricyanides, nitro-compounds, azo-compounds, indigo, nitriles, urea, and bodies of almost every class will, when suitably treated by this method, yield up their nitrogen in the form of ammonia, which is then determined volumetrically. Broadly speaking, the process consists in heating the substance with concentrated sulphuric acid which abstracts the elements of water, oxidises the carbon and is itself reduced to sulphur dioxide. This acts as a reducing agent on the nitrogenous matter, yielding, with the sulphuric acid present, ammonium sulphate. The ammonia is then liberated from the salt by boiling with caustic alkali, distilling it off into an excess of (a known volume of) standard acid, and determining the amount of acid which it neutralises by titration with standard alkali: from this the amount of nitrogen is found. The higher the temperature at which the sulphuric acid acts the easier will the oxidation take place and the process thereby be shortened. It is usual, therefore, to add powdered potassium sulphate to the sulphuric acid after the latter has acted on the material for some time and all frothing is over, thus obtaining a strongly acid solution of potassium hydrogen sulphate whose boiling point is much above that of the sulphuric acid itself. The addition of a globule of mercury, or a little precipitated mercuric oxide is recommended by some, to render the process still more rapid, but, if this is used, a subsequent addition of sodium or potassium sulphide is necessary, prior to distillation, to decompose any mercurammonium compounds that may be formed. When natural organic products are being analysed an excess of sulphuric acid should be employed.

The effect of the sulphuric acid is, as is explained above, to break up the body completely, [illegible] readily and in others after long continued boiling; but the complete conversion [illegible] nitrogen present as nitrates ("nitric" nitrogen) into ammonia ("organic" nitrogen) is not effected by the action of boiling sulphuric acid alone. Four cases therefore present themselves:

[illegible] *The determination of total nitrogen when there are no nitrates present.* The substance is treated as described in the sequel (**70**).

(b) *The determination of total nitrogen when there are nitrates present.* A slight modification [illegible] the first method serves to ensure the total nitrogen present in the substance being obtained in the form of ammonia. Salicylic acid or phenol is added to the sulphuric acid used for oxidation, preferably the former, in the proportion of about 40 grams to a litre of concentrated sulphuric acid. [illegible] mixture 30 c.c. is a suitable amount to employ with about 1 gram of the nitrogenous substance. The process of reducing the nitrates is facilitated by the addition of 2 or 3 grams of [illegible]st and a drop of mercury. Sodium thiosulphate has a similar effect. The action of the salicylic acid is to yield with the nitric acid of the nitrate a nitro compound, this being reduced to [illegible] amido compound which in the subsequent treatment with caustic alkali gives up its nitrogen in [illegible] ammonia.

[illegible] *Determination of "organic" nitrogen, including that present as ammonia, in the presence [illegible] "nitric" nitrogen.* To determine the former only, it is necessary that all nitric nitrogen should be removed from the solution. This can be done by heating the weighed substance containing nitrates with ferrous sulphate and concentrated hydrochloric acid, thus expelling all nitric acid. The residue is heated and the nitrogen determined as in **70**. Another method of getting rid of the nitrates is to add to the sample concentrated sulphuric acid containing formic acid in the proportion [illegible] c.c. of the latter (of s.g. 1.22) to 5 c.c. of the former. The formic acid is oxidised by the liberated nitric acid, first to oxalic acid and finally to carbon dioxide and water, the nitric acid becoming nitric oxide which is driven off on heating. The nitrogen can then be determined [illegible] **70**.

[illegible] *Determination of ammonia in free ammoniacal compounds, when nitrogenous organic matter* [illegible] [illegible]g's method should be employed for this. For detailed instructions see [illegible] *sixth edition.* [illegible]

70. Determination of nitrogen in the absence of nitrates.

[illegible] quantity of the substance (58) into a round-bottomed pear-shaped flask of hard [illegible] glass (special flasks with necks from six to ten inches long are made for this purpose) of about 500 c.c. [illegible] a drop of mercury, or about .5 gram of precipitated mercuric oxide. 20 or 30 c.c. of [illegible]

[illegible]

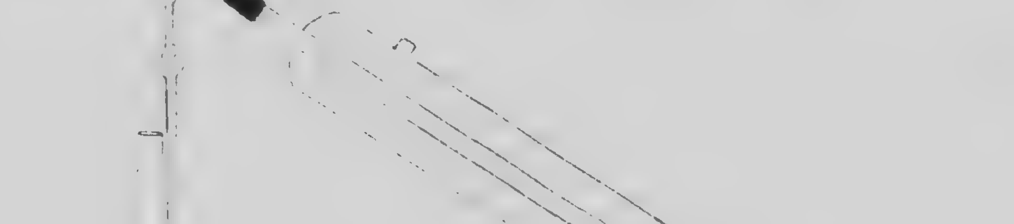
---

(58) The use of a large flask renders unnecessary the subsequent transference of the solution to a distilling flask.

concentrated sulphuric acid (free from nitrogen) (37) is poured in, the contents of the flask rotated to ensure thorough mixing, and heated in the fume cupboard, gently at first, gradually raising the temperature till the liquid boils briskly. After 10 or 15 minutes boiling the flame is removed, about 10 grams of dry powdered potassium or sodium sulphate added and the heating continued till the contents of the flask are clear and practically colourless. The flask should be inclined on one side and a loosely fitting stopper having a long end projecting inwards, or a small filter-funnel, inserted in its neck to obviate any loss through spirting

When the reaction is complete allow the flask and contents to cool, cautiously dilute the solution with about 250 c.c. of distilled water (ammonia-free) and drop in one or two pieces of granulated zinc or of broken pumice to prevent "bumping." At once attach the flask by means of a two-holed rubber stopper to a condensing apparatus such as that shewn in the figure. Through the tap-funnel in the second hole is introduced enough of a saturated solution of sodium or potassium hydroxide (free from nitrogen) to render the strongly acid mixture alkaline, following it with sufficient potassium sulphide solution (containg about 40 grams to the litre) to precipitate all the mercury or mercuric oxide, if that was previously added. Heat and distil off the ammonia into a measured quantity of decinormal sulphuric acid. (38) The excess of standard acid is then titrated as described in **29** with standard alkali of the same strength and the percentage of nitrogen in the sample [illegible]lculated from the amount of ammonia found

The figure illustrates how the distillation apparatus may be fitted up.(39) A block-tin condensing tube is better than a glass one, as the latter is acted upon to a slight extent by steam, yielding traces of alkali.



---

(37) All reagents must be carefully tested by blank experiments. About half a gram of pure cane sugar should be treated with the same quantities of sulphuric acid and other reagents that are to be used in the process and the amount of ammonia thus found taken into account in calculating the result of the determination.

(38) The first 150 c.c. of the distillate will contain practically all the ammonia, but the next portion, nevertheless, should be received in a beaker containing a little water and a drop of the indicator to be used in the titration. If there is any sign of its being alkaline, what is collected [illegible]

(39) Most laboratories possess a heating and distilling apparatus for performing several nitrogen determinations at the same time. Illustrations of these can be found in any dealer's catalogue

The use of the tap-funnel for the admission of the caustic alkali is not essential: it may be added directly to the solution, but then there is a danger of some ammonia being lost before the flask can be attached to the condensing tube

As alkali is apt to be mechanically carried over with the distillate, the tube should rise some twelve or eighteen inches before being bent over. Numerous forms of "traps," also, are made use of for this purpose. The adapter delivering the ammonia and water into the standard acid should be made pear-shaped (an inverted funnel works well, also) and should be immersed only a small distance under the surface of the acid: variations of pressure during distillation will then cause no "running back"

71. Determination of total nitrogen when nitrates are present.

Make up the solution of salicylic acid in concentrated sulphuric acid that is described in **69,** *b*, and pour quickly about 30 c.c. of this on to the substance whose total nitrogen it is desired to estimate: the rapid addition of the acid prevents the liberation of lower oxides of nitrogen, which would occur were the substance not completely covered by the salicylic-sulphuric acid mixture immediately.(40) Shake and add to the contents of the Kjeldahl flask, while still cold, 2 or 3 grams of zinc dust and about a gram of mercury and allow these to dissolve slowly before heating. Continue the determination from this point exactly as described in **70.**

(40) [illegible]

GRAVIMETRIC ANALYSIS

72. A short explanation of the principles underlying analyses done by gravimetric methods is given in **1**. The element or acid radicle is converted into some compound of known and constant composition—in some cases the element itself—which is then weighed. In the operations of solution, precipitation, washing, drying, ignition and final weighing, a substance is inevitably subjected to so many processes that some instructions as to manipulation are necessary at this stage, though an ounce of demonstration in the laboratory is worth many pounds of written directions; very little space, therefore, will be taken up in this way and what guidance is given here will require to be largely supplemented by the instructor.

73. Solution and Evaporation.

In preparing a solid for examination great care must be taken that none of it is lost in transference to the beaker or flask in which its solution is to be effected. If weighed on a watch-glass every trace of it must be washed into the flask by means of a *fine* jet of water from a wash-bottle. The student will find the work greatly facilitated by having a supply of hot water always in the wash-bottle, protecting the hands by a piece of towelling wound round and secured to the neck. The flask or beaker should be placed on wire gauze or on a sand-bath over a bunsen burner and possible loss of material through "spurting" in the course of heating to effect complete solution is best avoided by covering the beaker with a large watch-glass or, in the case of an Erlenmeyer (or other form of) flask, by inserting a filter funnel in its neck. All moisture or material that collects on the watch-glass or funnel is carefully rinsed into the flask with water from the wash-bottle after solution is complete. In heating on the sand-bath do not use too much sand in it; a thin layer is all that is required to ensure the uniform heating of the vessel placed on it. The level of the liquid in a beaker or flask must not be allowed to become too low or there is danger of cracking. In evaporating solutions in a porcelain basin drops are liable to be ejected on heating; this may be avoided by placing an inverted filter funnel of suitable size over it, the edge of the funnel resting on the walls of the basin above the level of its contents. Liquids often have a tendency to creep up the sides of the vessels in which they are boiled or evaporated and care must be taken to remove the crust that is formed in this way, as well as any liquid or solid matter that may adhere to the inverted funnel, along with its contents.

74. Precipitation. to convert a substance in solution into an insoluble one, is best done in a beaker having a lip and in *hot* solutions. After the addition of the precipitant the precipitate is well stirred and allowed to settle; a few more drops of the reagent are added to the clear liquid to make sure that precipitation is complete, but a large excess must be avoided. By stirring and boiling, precipitates assume a granular condition, settle more rapidly and are more easily filtered. *Hot solutions pass through a filter much quicker than cold ones.*

75. Filtration and washing precipitates. The beaker containing the precipitate and liquid is allowed to stand till the precipitate has settled, when the clear liquid is decanted cautiously on to the filter, previously wetted, by pouring it down a glass rod held against the edge of the lip, care being taken to disturb the precipitate as little as possible. The filter must not be filled too full; drops are prevented from finding their way down the outside of the beaker by a proper use of the glass rod. After most of the liquid has been decanted through the filter, hot water is added to the contents of the beaker which are stirred and heated to boiling once more. After settling, the liquid is again poured through the filter and the operation repeated two or three times: this is known as "washing by decantation." Finally the precipitate is transferred to the filter by means of a fine jet of water from the wash-bottle. Some of the precipitate is apt to adhere to the walls of the beaker and this can be removed by playing on it a stream of water from the wash-bottle and, at the same time, rubbing it off with a glass rod tipped with about half an inch of narrow rubber tubing: a rod thus armed is known as a "policeman." The final washing of the precipitate is done on the filter. Filtration is facilitated and losses through splashing are avoided by letting the end of the funnel rest against the edge of the vessel that is receiving the filtrate. The liquid and precipitate must never completely fill the filter-paper—the latter never more than half—and each lot of wash-water must be allowed to drain through before more is added. The final wash-water, as it runs through, is tested to see that it is free from all soluble matter, otherwise this would add to the weight of the precipitate and would also render inaccurate any subsequent determination in the filtrate

76. Drying precipitates. From what has been said in ¶ it will be seen that, in the majority of cases, precipitates after washing are dried, ignited and weighed until the weight is constant. The drying process takes considerable time but there are occasions when it may be dispensed with and the filter-paper and its contents directly ignited. When drying ovens are available in which to place the precipitate and funnel it is best to cover the latter with a piece of moist filter-paper on which may be previously written, as a safeguard against possible mistakes, the nature of the precipitate contained in it. A quicker method is to suspend the funnel over the chimney of an argand burner. Another way is to remove the filter paper and its contents carefully from the funnel and to lay it on its side (with an intervening sheet of paper) on a piece of glass placed on the upper part of a "hot-plate," easily made by bending a piece of sheet iron into the form of a rectangular parallelopiped, (like a shallow box lacking the ends). The lower side of this is heated gently by a bunsen burner, the air space between the iron surfaces preventing the paper being subjected to too high a temperature.

77. Ignition of precipitates. When dry, the precipitate is transferred to a weighed porcelain (or platinum) crucible — previously heated to redness and cooled before weighing — and the paper, with what of the precipitate adheres firmly to it, rolled up loosely and secured by taking a turn round it with a platinum wire fixed in a glass rod. The paper is held over the crucible and there burned, the remains of the precipitate and the ash of the paper being allowed to fall into it. The crucible is then placed on a pipeclay triangle and heated with a direct flame till all the unconsumed carbon of the paper is burned away; after being heated strongly for a few minutes it is cooled and weighed. In some cases the carbon of the paper exercises a reducing action on the precipitate: removing the precipitate as completely as possible from the paper as described minimises this action very considerably, but *if any reduction takes place the precipitate will not be uniform in composition and therefore wholly unsuitable for weighing.* As such cases occur in the examples that follow, instructions for dealing with them will be given.

TYPICAL EXAMPLES OF GRAVIMETRIC ESTIMATIONS

78. Determination of iron.

Ferrous-ammonium-sulphate, $(FeSO_4 (NH_4)_2SO_4 6H_2O)$ known as Mohr's salt, may be used for this estimation : before precipitation it requires to be oxidised to the ferric salt and afterwards converted into ferric hydroxide by the addition of ammonia.

Weigh out about a gram of the salt on a watch-glass and transfer it completely to a beaker ; cover with hot water to the depth of an inch or so and warm, adding a little concentrated nitric acid to oxidise the iron. A brown colouration will be produced owing to the reduction of the nitric acid and the absorption of the nitric oxide by the ferrous salt. Heating is continued until the addition of a drop of nitric acid causes no farther change. The complete oxidation of the iron to ferric salt may be confirmed by using a solution of potassium ferricyanide as an outside indicator in the manner described under **44**.

To the hot solution is added ammonia in excess, that is, till the solution smells strongly of this reagent, the mixture stirred with a glass rod armed with a rubber tip (**75**) and boiled till the greater portion of the ammonia is expelled. After the precipitate has settled, the hot liquid is cautiously decanted through a filter, the precipitate washed once or twice by decantation (**72**) and finally transferred to the filter where it is subjected still further to the washing process until the washings contain no trace of soluble matter.(41) In washing the precipitate on the filter it should be collected as far as is possible in a compact mass in the cone of the filter leaving the upper edges of the paper perfectly clean. After allowing it to drain for a few minutes, the filter with the precipitate is carefully removed from the funnel and laid on its side on a piece of paper resting on the hot-plate where it is dried. While the precipitate is drying, a porcelain (or platinum) crucible resting on a pipeclay triangle over a bunsen burner, is heated to redness, cooled,(42) weighed and placed on a piece of glazed paper on the table in readiness to receive the precipitate.

When dry, the precipitate is [illegible] by gently squeezing the filter paper and as much [illegible] possible transferred to the crucible, the paper being treated as described in **77**. Any particles [illegible] precipitate that have fallen outside the crucible can readily be gathered together on the glazed paper by means of a camel's hair brush or feather and added to the contents of the crucible which is then heated to redness for about [illegible] minutes, cooled and weighed.[illegible]

From this the quantity of iron is calculated as follows:

Weight of watch-glass .... grams
Weight of watch-glass + salt .... grams

Weight of salt taken .... grams.

(Here the student should enter a concise description of the operations carried out.)

Weight of crucible + Fe_2O_3 + ash .... grams
Weight of crucible .... grams

Weight of Fe_2O_3 + ash .... grams
Deduct weight of ash .... gram

Weight of Fe_2O_3 .... grams.

Calculating this to iron

Fe_2O_3 : Fe_2 = Wt. of Fe_2O_3 found : x grams iron in sample

or

x = Wt. of Fe_2O_3 found × $\frac{112}{160}$ grams.(44)

Therefore, the percentage of iron = x × $\frac{100}{\text{Wt. of sample}}$.

The student should compare this result with the theoretical percentage of the element in the salt used for analysis. Mohr's salt being $FeSO_4 (NH_4)_2 SO_4 6H_2O$, molecular weight 392, the percentage of iron in it, x, is found from the proportion

$$392 : 100 = 56 : x$$

$$x = \frac{56 \times 100}{392} = 14.2\%$$

---

(41) The soluble matter in contact with the precipitated $Fe(OH)_3$ in this case is ammonium sulphate, and may be tested for by collecting a few c.c. of the washings in a test tube and adding $BaCl_2$ which will cause a milkiness, due to $BaSO_4$, as long as there is any salt present.

(42) Where one is available, a desiccator should be used in which to cool crucibles and to carry them backwards and forwards between the [illegible]

(43) [illegible] Fe_2O_3 that may be reduced by the paper to metallic iron is reconverted into oxide [illegible]

(44) See **2**. The fraction $\frac{112}{160}$ is the "factor" for calculating Fe_2O_3 to Fe. Many books supply these factors, with litt[illegible]

79. Determination of aluminium.

[illegible] 78 [illegible]

[illegible] 78 [illegible] Al_2O_3 [illegible] 78. [illegible]

80. Determination of chromium

[illegible] 78 [illegible] 79 [illegible]

81. Determination of copper by weighing as oxide.

Non-volatile organic substances, such as tartaric acid and sugar, [illegible] as also of the hydroxide of other metals.

[illegible]

[illegible] copper oxide [illegible] copper [illegible]

[illegible] percentage [illegible] copper in $CuSO_4,5H_2O$ [illegible]

82. Determination of sulphuric acid (''SO_4), in a soluble sulphate.

The sulphuric acid radicle is converted into insoluble barium sulphate ($BaSO_4$) by precipitation [illegible]

[illegible]

[illegible] from the paper as completely as possible and removed to a [illegible] BaS [illegible] BaSO4. [illegible] sulphuric acid [illegible] until the acids and moisture are expelled [illegible] from the weight of BaSO4 the [illegible] may be calculated.

83. Determination of lead as sulphate (PbSO4).

[illegible]

[illegible] this precipitate is to remove it from the paper [illegible] and to burn the paper in an inverted crucible lid. [illegible] burned off and the lid allowed to cool, is moistened with a [illegible] before and the acids cautiously expelled by heat. Crucible and lid are then heated together, cooled and weighed.

84. Determination of magnesium.

Magnesium sulphate ($MgSO_4 \cdot 7H_2O$) may be used for this estimation. The magnesium is precipitated as **$MgNH_4PO_4 \cdot 6H_2O$**, a crystalline precipitate, by the addition of sodium phosphate (Na_2HPO_4) to solutions of magnesium salts containing ammonium chloride and ammonia. The reaction may be represented thus:

$$MgSO_4 + NH_4HO + Na_2HPO_4 = \mathbf{MgNH_4PO_4} + Na_2SO_4 + H_2O$$

Ammonia in excess of that required by this equation must be present, as the double phosphate is slightly soluble in water but insoluble in the presence of free ammonia. If ammonium chloride is not added first, the ammonia will precipitate the magnesium as hydroxide (**$Mg(OH)_2$**); sufficient ammonium chloride must therefore be present to prevent this occurring.(23) The precipitate on ignition becomes the pyrophosphate (**$Mg_2P_2O_7$**) in which form it is weighed, and from this the magnesium [illegible]

Dissolve about 1 gram of magnesium sulphate in water [illegible] after the [illegible] ammonium chloride present. [illegible] *in contact with the walls of the beaker* [illegible] cover the beaker and allow it to stand for at least [illegible] filter and wash the precipitate [illegible] 83; [illegible] add the precipitate to the ash, ignite once more [illegible] flame and finish off the ignition with the blow pipe. Cool and weigh. Heat again to weight constancy.

[illegible]

(23) [illegible]

$$[illegible] NH_4HO = \mathbf{Mg(OH)_2} [illegible]$$

$$\mathbf{Mg(OH)_2} + 4NH_4Cl = 2NH_4HO + [illegible]$$

[illegible]

85. Determination of calcium

[illegible] ammonia. The [illegible] may be collected on a tared filter, dried at [illegible] and weighed as $CaC_2O_4.H_2O$. It is more usual, however, to ignite the precipitated oxalate and [illegible] [illegible] conversion into oxide is complete and weigh it in that form. An accurate and quicker method is to determine the precipitated calcium oxalate volumetrically [illegible] titration with potassium permanganate, **(41)**

[illegible] salt (best obtained by dissolving about 1 gram of calcium [illegible] hydrochloric acid, keeping [illegible] watch-glass to prevent loss by effervescence) add enough ammonia to [illegible] [illegible] excess of a boiling solution of ammonium oxalate $(NH_4)_2C_2O_4$ [illegible] the [illegible] ammonia by decantation first and finally on the filter [illegible] Take care that every particle of precipitate is transferred to [illegible] rubbing with a policeman to ensure its removal [illegible]

[illegible] $CaCO_3$ [illegible] the filter and remove the precipitate as completely [illegible] [illegible] Evaporate [illegible]

[illegible] CaO. This is more expeditious and requires less patience than a. [illegible] [illegible] in a crucible and heat cautiously at first to drive off the water [illegible] [illegible] for 10 or 15 [illegible] the weight [illegible]

[illegible] **39**, **40** and **41**

[illegible]

86. Estimation of phosphoric acid in a soluble phosphate.

Phosphoric acid, (H_3PO_4), is precipitated as $MgNH_4PO_4.6H_2O$, ignited and weighed as $Mg_2P_2O_7$. [illegible] that this is the converse of **84**; the principle is the same but a soluble magnesium salt is the precipitatant. From the weight of the pyrophosphate the desired calculation can be made.

[illegible] magnesium ammonium phosphate has begun to form. [illegible] the precipitate as described in **84**.

87. Determination of cupric and ferrous sulphates when mixed.

[illegible] separated from the iron by means of hydrogen sulphide which [illegible] CuS, the copper sulphide is next converted into the oxide CuO, in which form it is weighed [illegible]

a. Determination of copper.

To a known amount of the mixture, in an Erlenmeyer flask, add about [illegible] c.c. of water and 15 c.c. of dilute hydrochloric acid; heat and pass hydrogen sulphide gas through the solution till, on boiling and allowing the precipitate to settle, the supernatant liquid appears colourless. (Wash everything that adheres to the delivery-tube carefully into the flask also.) Allow to settle and decant through a filter; wash with hot water once or twice by decantation and finally transfer the precipitate to the filter and wash thoroughly.

Carefully label and put aside the filtrate and washings, which now contain ferrous sulphate and an excess of hydrogen sulphide; treat this as detailed under **b**.

To obtain the copper in a convenient form for weighing, pierce the peak of the filter paper with a glass rod and wash the precipitate, together with that which adheres to the glass rod, through into a beaker placed underneath. Wash also the filter paper and funnel with a little hot dilute nitric acid to ensure complete transference of all copper compounds to the beaker. Warm the mixture and add as much concentrated nitric acid as is required to dissolve the copper sulphide completely and no more. *Excess of nitric acid must be avoided.* As solution progresses sulphur will separate and will appear black owing to the undecomposed copper sulphide which it encloses. Heating with nitric acid must be continued until every trace of black has disappeared and no insoluble matter remains but a little sulphur. This usually is in the form of a compact mass; it is removed mechanically from the solution, washed free of adhering solution and the washings added to the contents of the beaker.

The solution now contains copper nitrate and an excess of nitric acid. Add potassium hydroxide solution [illegible] excess and proceed as directed in **87.** Calculate the copper found to $CuSO_4 5H_2O$

b. Determination of iron.

The filtrate from the copper sulphide precipitate is now boiled until all hydrogen sulphide is expelled: the point can be ascertained by testing from time to time with a strip of filter-paper moistened with a solution of a lead salt. When quite free from hydrogen sulphide, cool the solution under the tap *at once* and then titrate with $\frac{N}{10}$ permanganate as explained in **35**. Calculate to $FeSO_4 7H_2O$

c. Determination of (SO_4).

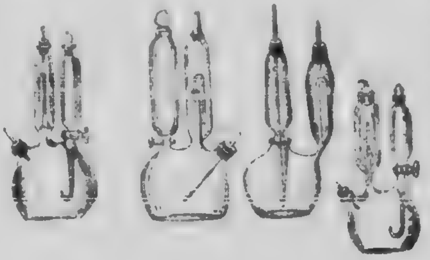
The copper and iron present in the mixture of sulphates having been determined, there only remains now the estimation of the SO_4. To do this, take a fresh sample of the substance under examination, acidify slightly with dilute hydrochloric acid and proceed as laid down in **82.**

88. Determination of carbon dioxide in a carbonate.

This can be done either by determining the loss in weight sustained by an apparatus containing the carbonate and the acid necessary to decompose it, after the action has taken place and the carbon dioxide has been expelled, or by directly weighing the carbon dioxide evolved when the carbonate is treated with dilute acid.

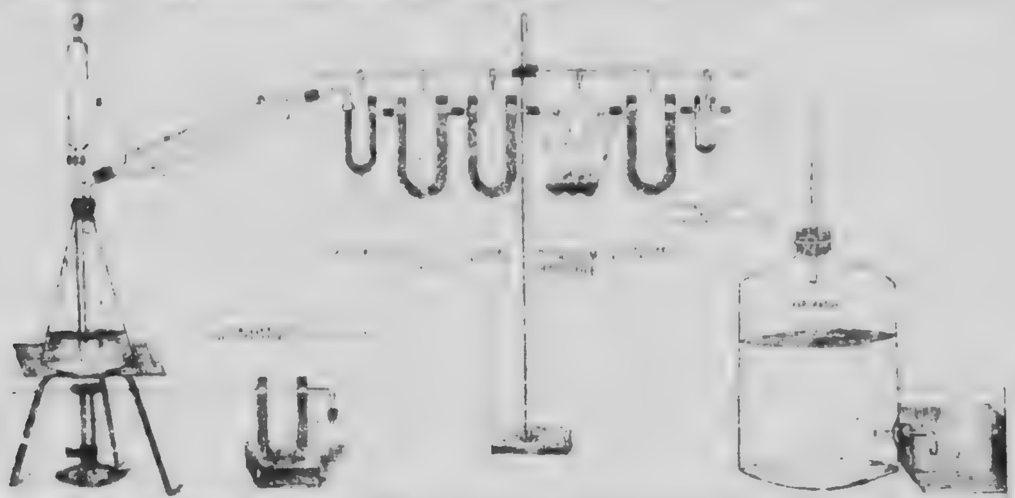
89. Determination by difference.

Numerous forms of apparatus have been devised for this purpose, a few of which are illustrated. The principle of each is the same: a known weight of the sample is placed in the bottom of the apparatus, dilute hydrochloric acid is put in the stoppered funnel and concentrated sulphuric acid half fills the exit-tube to dry the escaping carbon dioxide. The whole apparatus, with its contents, is weighed, the acid allowed to run in slowly and, when effervescence has ceased, heat is applied till all carbon dioxide has been driven out through the sulphuric acid trap. Carbon dioxide-free air is then sucked or forced through till the carbon dioxide is completely removed, when the apparatus is cooled and weighed. The gas must not escape too quickly or it will carry water vapour with it: only 2 or 3 bubbles per second should pass out through the sulphuric acid



90. Determination by direct weighing.

The [illegible] and is absorbed by [illegible]. [illegible] Under these circumstances hydrochloric acid must be employed [illegible] the advantage of being volatile. If the sample is suspended in water and hydrochloric acid added [illegible] gaseous hydrochloric acid and, if the ca[illegible] [illegible] hydrogen [illegible]. Arrangements are therefore made for absorbing these before they can reach the weighed tube containing the potassium hydrate [illegible] in the figure. [illegible] quantity is placed in the flask *A*, is decomposed



by slowly running in dilute hydrochloric acid from the dropping funnel *B*, the extremity of which [illegible] with its end turned upwards to prevent gas-bubbles entering, dip [illegible] the level of the liquid. The air in the flask and the carbon dioxide pass out through the [illegible] condenser *C* which prevents part of the water vapour from going any further. Tube *D* (containing granulated calcium chloride) frees the gas from moisture and tube *E* (containing fragments of pumice-stone previously saturated with copper sulphate by boiling with a [illegible] solution of that salt and afterwards heating to dehydrate the copper salt) removes any hydrochloric acid gas and hydrogen sulphide. *F* ensures complete purification of the gas before it [illegible] shown in the figure, with potassium hydroxide solution (equal parts of [illegible] water is a suitable concentration) and in which the [illegible] *H* retaining any that may escape absorption in the potash-bulbs. *H* is filled [illegible] of its length with soda-lime and the remaining [illegible] with granulated calcium chloride; the latter [illegible] that may evaporate from the soda-lime, the temperature of which rises considerably [illegible] smaller tube containing sufficient concentrated [illegible] to just stop it up and serves two ends: it indicates the rate at which the [illegible] passing through the apparatus and it prevents any moisture finding its way into the weighed tubes from the aspirator *K*. The tube *L* contains soda-lime and has a connection ready to insert into the mouth of the funnel *B* after the reaction between the carbonate and the acid has ceased when air, free from carbon dioxide and moisture, is drawn through the system to drive all carbon dioxide contained in it into the absorption tubes *G* and *H*. *L* and *K* are not connected [illegible] stage of the experiment.

The various connections are explained by the figure. The **U** tubes are filled almost up to [illegible] tubes, a loose plug of glass-wool being inserted between the granular absorbe[illegible] and the latter to prevent any solid matter entering them. On the ends of the side tubes are fitted short lengths of rubber tubing, each closed at the end by a small piece of glass-rod, to protect their contents from the atmosphere. When an experiment is commenced the glass stoppers are removed and the rubber serves to connect the tubes. All joints and corks should be lightly paraffined and the whole apparatus must be perfectly gas-tight before it is used. To test if this is so, insert the cork at the end of the air-purifying tube *L* into the neck of the dropping funnel *B*. Attach a long piece of glass tubing to the side tube of *I*, letting the other extremity of it stand in a beaker of water. Then apply gentle suction when the water from the beaker will rise in the tube; close the tap of the funnel and leave it to stand. If the level of the water and the level of the solution in the potash-bulbs remain stationary for about 10 minutes the apparatus is air-tight. If not the leak must be found and remedied.

[illegible] of absorbing the carbon dioxide in a solution of alkaline hydroxide, some workers prefer using soda-lime. In place, therefore, of the potash-bulbs *G*, a U tube, charged similarly to *H*, is inserted. This substance, being in the form of a granular powder, presents a large surface to the action of the carbon dioxide, and its conversion into carbonate is accompanied by a considerable amount of heat. So much so, indeed, that the guard tube *H*, becomes a necessity, intercepting any moisture originally present in the weighed soda-lime tube that may be expelled during the high temperature the latter attains. The soda-lime is carefully sifted before use in order to remove the dusty portion which might tend to retard the passage of the gas. The heating and subsequent cooling of these tubes also serve as a useful guide to the progress of the absorption.

To perform the estimation, weigh from 1 to 5 grams of the powdered sample into the flask *A* and add water sufficient to cover the turn-up end of *B* when inserted. Remove the end stopper from *I*, half fill *B* with dilute hydrochloric acid (conc. HCl 1 part, water 1 part) and allow it to run into the flask [illegible]. *The operation must be so performed that the carbon dioxide is* [illegible] *and passes through the purifying and absorbing system sufficiently steadily to ensure complete absorption* [illegible] *current.* When all effervescence has ceased circulate cold water through the condenser, attach the air [illegible] tube (or tower) [illegible] the funnel *B*, allow the remainder of the acid in *B* to run into the flask, connect [illegible] aspirator *K* to *I* and draw a slow current of air through the whole apparatus. Cautiously heat the contents of the flask to incipient boiling and keep the air current steady. When a sufficient time has elapsed remove the source of heat and increase the air current, keeping it going for about 10 minutes.

Remove the absorption vessels *G* and *H* to the balance, taking care to close their ends with the rubber tubes and glass stoppers, cool and weigh. The increase in weight is the carbon dioxide.

PART II

THE ANALYSIS OF JEWELRY MATERIALS AND MANUFACTURED PRODUCTS

LIMESTONE OR DOLOMITE.

Limestone is essentially calcium carbonate, but generally contains magnesium carbonate; the presence of any considerable quantity of the latter causes the rock to be classed as a dolomite. Other constituents of the rock which are almost always present and which must be determined, are iron, aluminium, silica and phosphorus. The silica is generally in combination with the bases in the form of silicates insoluble in hydrochloric acid, though free silica in the form of quartz may be present also. Differentiation of the combined and free silica is sometimes desirable as it gives valuable information regarding the origin of the deposit. Phosphorus, when present, will be in combination with the metallic elements as phosphate.

91. The ***general plan of the analysis*** is as follows:- By treatment with hydrochloric acid separate into a soluble and an insoluble portion.

92. ***In the soluble portion.*** (1) Determine *iron and aluminium* together by precipitation with ammonia; weigh as Al_2O_3 and Fe_2O_3, (**78**). If desired, the proportions of these combined oxides can be estimated, (**109-111**).

(2) In the filtrate from the iron and aluminium precipitate, determine the *calcium* by precipitation with ammonium oxalate, (**85**).

(3) In the filtrate from (2), determine *magnesium* by precipitation with sodium phosphate, (**84**).

(4) In the soluble portion of a fresh sample, determine *phosphorus*.

93. ***In the insoluble portion*** (*) (1) Determine *total silica* by fusion with alkaline carbonates, treatment with hydrochloric acid and dehydration. Weigh as SiO_2, (**98**).

(2) In the filtrate from the silica, determine the same metals as in the soluble portion and by the same methods.

In another sample of the mineral, determine the *carbon dioxide*, (**88-90**).

94. Weigh out from 1 to 2 grams of sample (dried at 100°) into a small beaker. Cover with a watch-glass to prevent loss by effervescence and introduce through the lip, by means of a pipette, from 15 to 20 c.c. of dilute hydrochloric acid. After the first violence of the effervescence has subsided, warm gently on a water or sand bath to complete the solution, adding a little concentrated hydrochloric acid if necessary. Evaporate to dryness, and to the dry mass add 10 c.c. of dilute hydrochloric acid, and about [illegible] c.c. of water; filter through a small filter-paper, and wash well with hot water (about 100 c.c. of wash water, properly used, should be ample). The soluble portion contains the greater part of the iron, aluminium, calcium and magnesium. The residue on the filter consists of silica and insoluble silicates of the above metals.

Analysis of the Soluble Portion.

95. ***Determination of Iron and Aluminium.*** Heat the solution almost to boiling (the addition of a few drops of concentrated nitric acid may be necessary to oxidise the iron present), then add ammonia slowly, in slight excess. Stir well and boil for about 3 minutes. Filter, and wash the precipitate with hot water. The ammonia precipitates the hydroxides of iron and aluminium, which bring down with them a small quantity of calcium and magnesium. To free the precipitate from the latter, dissolve it off the paper into a clean beaker with as small an amount as possible of hot dilute hydrochloric acid. Wash the paper well with hot water. Dilute this solution to about 150 c.c., and precipitate with ammonia as before. Filter, and wash with hot water. This filtrate should be combined with that from the first precipitation. Then treat the precipitate as in **78** or place the filter-paper with the combined hydroxides in a crucible while still moist, and heat cautiously at first but finally with the blow-pipe for about 5 minutes. Cool and weigh as Fe_2O_3 and Al_2O_3 (**)

96. ***Determination of Calcium.*** The combined filtrates from the precipitation of iron and aluminium should be boiled down till the volume does not exceed 300 c.c. To the almost boiling solution add 5 c.c. of ammonia and then a slight excess of a boiling solution of ammonium oxalate. Continue to boil until the precipitated calcium oxalate becomes granular, set aside for an hour, filter and wash a few times with hot water. Ignite the precipitate and filter-paper in a platinum crucible; cool, and redissolve the calcium oxide in dilute hydrochloric acid, making the solution up to about 100 c.c. Again precipitate the calcium as oxalate by the addition to the boiling solution of ammonia and ammonium oxalate in excess, and treat as in **85**.

(*) [illegible] may be dried at 100° and weighed. It generally consists of separated silica, clay, sand and organic matter. Where it is desired to determine the organic matter in a limestone, a convenient approximate method is to filter, after dissolving the sample, through [illegible] papers, wash with hot water, dry the papers at 100°, and weigh; incinerate the filter carrying the insoluble residue, including [illegible], and weigh again. The loss in weight gives directly the amount of organic matter. The usual fusion is then made on the inorganic matter.

(**) It is seldom necessary to determine what proportion of these combined oxides is Fe_2O_3 and what is Al_2O_3. When necessary, however, [illegible] may be [illegible] precisely as given under Clay (**109-111**).

97. Determination of Magnesium [illegible] **84** [illegible]

Analysis of the Insoluble [illegible]

98. Determination of Silica [illegible]

99. Analysis of filtrate from Silica [illegible]

100. Determination of Phosphorus [illegible] **95** [illegible]

[illegible] **94** [illegible]

when agitated: if this point is passed, a few drops of dilute nitric acid may be added, and then more ammonia if necessary. The solution should now have the dark brown colour of neutral [illegible] or the light yellow of acid ferric solutions; it should be perfectly clear and should not exceed [illegible] in volume. Heat the solution till it is as many degrees *above* 60 as the laboratory temperature is [illegible]. Add to it an equal volume of an acid solution of ammonium molybdate[1] which must be at the temperature of the laboratory. Stopper the flask firmly, wrap in a towel and shake vigorously for five minutes, then allow to settle for the same space of time. Filter quickly through a small fine-grained paper, and wash by decantation with an acid solution of ammonium sulphate[2] till 5 c.c. of the washings give no colouration with dilute hydrogen sulphide water. When this point is reached, discontinue the washing and place the flask, which will still contain most of the precipitate, beneath the funnel. Pour 12 c.c. of dilute ammonia over the filter, to dissolve the ammonium phospho-molybdate; run this into the flask, wash the paper carefully with 100 c.c. of water and, if necessary, add a little more ammonia till a clear solution is obtained. Transfer this solution to a beaker and make it faintly acid with dilute hydrochloric acid: then add a crystal of tartaric acid, make alkaline again with dilute ammonia and allow to [illegible].

Next add Magnesia Mixture and complete the estimation as insructed in **86**.

101. *Should Manganese be present* it [illegible] be estimated as described under Haematite, ***132***

102. *Determination of Carbon Dioxide* This is done as described in ***88-90***

CLAY.

Clay is formed by the disintegration of rocks containing silicates of aluminium and consist [illegible] mixture of real clay with quartz-sand, containing varying amounts of compounds of iron, calcium, magnesium, and the alkalies.

103. The following are usually estimated, being the most important constituents, and the proportions of which determine the character of the rock. $-SiO_2$, Al_2O_3, FeO, Fe_2O_3, MgO, CaO, Na_2O, K_2O, combined water, and carbon dioxide.

104. [illegible] coarse [illegible] sand [illegible] separated [illegible] the clay.

105. The ***general plan of the analysis*** may be outlined thus:

(1) Determine the *silica* by fusion with mixed carbonates, ***106, 107***

(2) In the filtrate from the silica, determine *iron and aluminium*, ***108***

(3) In the mixed oxides of iron and aluminium, determine the *iron*, ***109-111***

(4) In the filtrate from the iron and aluminium precipitate, determine the *calcium*, ***112***

(5) In the filtrate from the calcium, determine the *magnesium*, ***112***

(6) A fresh sample of the clay is decomposed by heating it with its own weight of pure ammonium chloride and eight times its weight of precipitated calcium carbonate. The water soluble portion of the fusion contains the alkali metals and calcium in the form of chlorides. The calcium salt is removed by precipitation with ammonia and ammonium carbonate, the ammonium compounds expelled by heat and the mixed chlorides of potassium and sodium weighed. In the combined chlorides the *potassium* is precipitated and weighed as potassium chloroplatinate: the *sodium* is thus determined by difference, ***113, 114***

(7) In a separate portion, determine the *combined water*, ***115***

(8) In a separate portion, determine the *carbon dioxide*, ***116***

(9) In a separate portion, determine the amount of *iron present in the ferrous condition*. This is done by decomposing the rock in a sealed tube, by means of sulphuric acid. The solution is subsequently washed from the tube and titrated with potassium permanganate, ***117***.

106. *Fusion and solution* The clay should be finely ground until when rubbed with the fingers no gritty particles are felt: it is dried at from 100° to 110° to constant weight.

---

[1] [illegible] molybdate [illegible] grams of molybdic oxide in 300 c.c. of dilute ammonia (Sp. Gr. [illegible]) and add slowly with constant stirring, to 300 c.c. of nitric acid (Sp. Gr. 1.2). Warm to 45° and add [illegible] c.c. of a 10% solution of sodium [illegible] [illegible] the saturation of the reagent with the phospho-molybdate. Stand in a warm place over night. The solution [illegible] [illegible] that salt, as commonly sold, is not of certain composition; its use for the purpose is therefore not advisable.

[2] [illegible] made by adding to 500 c.c. of water, 27.5 c.c. of dilute ammonia (Sp. Gr. 0.96) and 24 c.c. of concentrated sulphuric [illegible]

[illegible] precipitates [illegible] *124* [illegible] one gram of clay into an agate mortar and grind it up till mixed thoroughly with five [illegible] fusion mixture (mixed carbonates, see note [illegible]). [illegible] the mixture into a large platinum [illegible], rinsing out the mortar by rubbing [illegible] an additional amount (not exceeding 1 gram) of [illegible] mixture. The operation must be carefully performed over a sheet of glazed paper, in order that no loss may take place. Fuse thoroughly, and when cool transfer the crucible and contents to [illegible] moderately deep porcelain basin or casserole of about 15 cm. diameter. With the aid of a [illegible] jet of hot water from a wash-bottle, and repeated small additions of hydrochloric acid, remove the fused mass from the crucible, and completely decompose the carbonates by further [illegible] of dilute hydrochloric acid. Remove the crucible and thoroughly wash it with hot water, rubbing [illegible] at the same time with a policeman to remove adherent silica. Evaporate the contents of the casserole on the water-bath, spreading the pasty substance over as large a surface as possible.

107. Determination of Silica. Heat the contents of the vessel in an air bath for two hours between 105° and 115°, stirring from time to time in order to granulate the mass. When cool, add 10 c.c. of dilute hydrochloric acid and enough hot water to completely dissolve the [illegible]. Filter, and treat as described under Dolomite. **98**

108. Determination of Iron and Aluminium. Dissolve in a little nitric acid, any [illegible] silica, boil the solution, add [illegible] ammonia till the solution is alkaline. Allow the precipitate to settle [illegible] decant the clear [illegible] and wash the precipitate with hot water by decantation, then finally, with great care, on [illegible] paper. Redissolve in hot hydrochloric acid and repeat the precipitation and washing. (The [illegible] and washings from the two precipitations are used for the determination of Calcium [illegible] Magnesium. **112**) Dry the precipitate, separate it from the paper, ignite the latter [illegible] crucible, add the former, and re-ignite using the flame of the blow-pipe. [illegible] Cool and weigh the [illegible] Fe_2O_3 and [illegible]

109. Determination of Iron. The total amount of iron in the combined ferric and aluminium oxides must now be determined, after which the amount of aluminium is found by difference. The ignited precipitate of Fe_2O_3 and Al_2O_3 is seldom readily soluble in hydrochloric [illegible] adopted. Place in the crucible (which should be [illegible] large one), containing the ignited and weighed precipitate, [illegible] grams of potassium pyrosulphate [illegible] potassium hydrogen sulphate), and heat gently with the flame of a bunsen [illegible]. The temperature should be so regulated that the mass is just kept liquid, and a slight [illegible] of sulphur trioxide is noticed, but should be as low as is consistent with these [illegible] being maintained. A fair degree of watchfulness is necessary, or loss may be occasioned by [illegible] heating, and the projection of its contents from the crucible. When the fusion is complete (the fused mass should be clear and free from floating matter), allow the crucible to cool, [illegible] in such a way as to make the mass solidify round the sides rather than as a solid cake at the bottom. Place the crucible in a beaker and add enough water and dilute sulphuric acid to completely dissolve its contents.[illegible] Warm the solution almost to boiling and pass hydrogen sulphide gas into it till no further precipitation of sulphur (or platinum sulphide) takes place. Cover the beaker and allow it to stand for a few hours (this renders the platinum sulphide easier to filter out), then boil and again pass in hydrogen sulphide to completely reduce the iron. Filter, while hot, into a flask through which a stream of carbon dioxide is being passed, boil to expel all hydrogen sulphide (continuing meanwhile to pass in carbon dioxide), cool and then titrate the [illegible] with [illegible] permanganate. The hydrogen sulphide used must be very carefully washed [illegible] traces of iron may be carried over from the generator.

[illegible]

[illegible] the precipitate and [illegible] this treatment until it has been sufficiently washed by decantation. As [illegible]

[illegible]

110. Another method for the determination of iron in the precipitate is as follows:—Fuse as before with potassium pyrosulphate and dissolve the contents of the crucible in water containing a definite amount of dilute sulphuric acid. Pass the solution slowly through a Jones reductor,[illegible] and wash the reductor with 150 c.c. of water. Titrate the solution in the reductor flask with potassium permanganate. It is usually necessary to make a blank determination with the reductor, immediately before or after, using the same volumes of liquid, sulphuric acid and wash water.[illegible]

111. Yet another method is as follows: Fuse the mixed oxides of iron and aluminium with potassium pyrosulphate, extract the fused mass with dilute sulphuric acid, filter if necessary and reduce the ferric iron to the ferrous condition by bubbling sulphur dioxide through the solution. (Should sulphur separate filtration is advisable.) Transfer the solution, which must smell strongly of sulphur dioxide, to a conical flask provided with a cork and delivery tube bent over at right-angles. Clamp the flask to a retort stand and boil off the excess of sulphur dioxide, inserting the end of the delivery tube (when all the sulphur dioxide is apparently expelled) under the surface of a dilute solution of potassium permanganate contained in a test-tube held in the hand. As soon as the permanganate is no longer decolourised by the issuing gas, the flask and contents are cooled under the water-tap and the iron titrated with potassium permanganate.

112. ***Determination of Calcium and Magnesium.*** These elements are determined in the filtrate from iron and aluminium as described in ***96*** and ***97***.

113. ***Determination of the Alkalies.*** For this the clay must be ground to an impalpable powder. Weigh 0.5 gram into an agate mortar, add to it the same amount of pure ammonium chloride and grind the two together till they are thoroughly mixed. Next weigh out 4 grams of pure calcium carbonate,[illegible] add the greater part of this to the contents of the mortar and grind these till the mixing is complete. Transfer the mixture, by means of a brush and a sheet of glazed paper, to a platinum crucible of from about 20 to 30 c.c. capacity;[illegible] rinse out the mortar with the remaining portion of calcium carbonate and place these rinsings in the crucible. Cover it loosely and apply the flame of a bunsen burner with great care so that the lower third, but no more, of the crucible is kept at a dull red heat. To aid in regulating the temperature it is very convenient to fit the crucible into a hole cut in an asbestos board, so that the upper portion is protected from the direct heat of the flame: or it may be embedded in calcined magnesia contained in a larger crucible and the heat applied to the latter. When the smell of ammonia is no longer perceived to proceed from the contents of the crucible, the heat may be slightly increased and should be continued for an hour. The mass should by this time have completely sintered together, but should not have been allowed to fuse into a solid cake. Place the crucible with its contents in a porcelain vessel and extract it thoroughly with boiling water. Filter and wash, at first by decantation. Should the residue contain any large lumps which do not easily disintegrate, they may be carefully transferred to an agate mortar, broken up, and washed back with hot water. The alkali metals and calcium, in the form of chlorides, will be found in the clear solution. It is well to test the residue by dissolving it in hydrochloric acid. Should it not dissolve from the filter completely, it would indicate that the mineral had not been entirely decomposed by the fusion.

Boil the solution, now containing the chlorides of calcium and the alkali metals, in a porcelain vessel, add 10 c.c. of ammonia and a slight excess of a freshly prepared solution of ammonium carbonate. Filter the solution into a platinum dish. Dissolve the precipitate in a slight excess of

---

[illegible] The Jones Reductor consists of a glass tube, about [illegible] The latter passes through a [illegible] narrow end is placed a light plug of glass-wool and the tube is [illegible]

To reduce a solution by means of this apparatus attach [illegible] of concentrated sulphuric acid, pour it into the reductor tube till the [illegible] the flask so that the solution passes in a slow stream into it. [illegible] wash-water, regulating the addition of the solution and washing [illegible] reductor till the washing is completed. (This precaution is necessary [illegible] reductor, if it has been allowed to stand, it should be well washed by passing [illegible]

Should the zinc used contain any appreciable trace of iron [illegible] before the real analysis. The same volume of liquid of the same acidity as the solution to be analysed [illegible] amount of iron taken up and consequently the amount of permanganate [illegible] has been passed through. It is an advantage to have the zinc amalgamated [illegible] much used since last it was charged. To do this, wash it [illegible] mercurous nitrate dissolved in 500 c.c. of water and 2 or 3 c.c. of nitric acid. Stir the zinc [illegible] wash repeatedly with water, then with water slightly acidified with hydrochloric acid and finally with [illegible]

[illegible] to this method for the following reason: Should [illegible] titanium be present in the [illegible] reduced and oxidised at the same time as the iron. If any error is to be encountered through the presence of titanium, it is [illegible] made to fall on the aluminium rather than on the iron determination. Apart from such objections this method of determing iron is excellent.

[illegible] The calcium carbonate and ammonium chloride should be specially prepared and used for this purpose only. Even when the greatest care is taken in their preparation they will not be entirely free from alkali and a blank determination should be made on each new sample.

[illegible] A thin layer of calcium carbonate placed in the bottom of the crucible before the mixture is added will prevent the fusion adhering to [illegible]

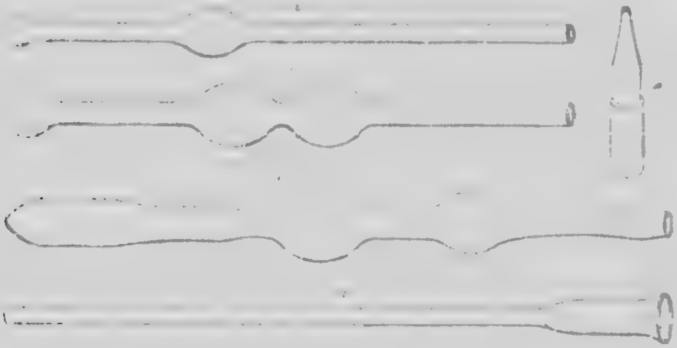
[illegible] filtrate to the [illegible] and evaporate to dryness on the water bath. Ignite the residue very cautiously over a small [illegible] to drive off the excess of ammonium salts. A trace of calcium will almost certainly have escaped precipitation by the ammonium carbonate; it is removed in the following way. [illegible] from the expulsion of ammonium salts in about 10 c.c. of water, add two drops of ammonia [illegible] filter through a very small filter into a weighed [illegible] dish. Wash the paper thoroughly with hot water, evaporate the filtrate to dryness [illegible] concentrated hydrochloric acid, again [illegible] Weigh the [illegible] contents, which will now consist of the combined [illegible]

114. Determination of Potassium

Dissolve the combined chlorides obtained as [illegible] Add [illegible] excess of [illegible] platinic acid, warm on the water-bath, adding enough warm water to redissolve the [illegible] chloroplatinate, and evaporate till the residue becomes pasty. Add 30 c.c. [illegible] with alcohol of the same strength [illegible] small filter. The washings should at first be yellow, and the process may be [illegible] they become entirely colourless and the filter-paper is free from yellow stains. [illegible] the greater part of the precipitate on the water-bath, and transfer the [illegible] with the aid of a fine camel's hair brush to a small weighed crucible. Dissolve in boiling water any precipitate which cannot be removed in this way and any adhering to the filter. [illegible] this solution also into the crucible, evaporate on the water bath, dry for half an hour at 130° in air-bath, and weigh the crucible and potassium chloroplatinate (K_2PtCl_6).

115. Determination of Water

It will be evident at once that only when a rock is free from fluorine, chlorine, carbon, carbon dioxide, and oxidisable or reducible bodies can the water be determined by "loss on ignition." To obtain anything like accurate results the water driven [illegible] this may be done in absorption tubes of various kinds but a [illegible] and simple method is that of Penfield,[1] in which the rock is heated at one end of a [illegible] illustrated in the figure. The enlargements in the middle collect the water and prevent it running back and causing a fracture at the heated portion. Escape of steam during the ignition, due to air currents, can be prevented by fitting a short tube, drawn out to a capillary point, over the open end of the Penfield tube by means of a small piece of rubber tubing. Thoroughly dry the tube by heating it and aspirating dry air through it, then cool and weigh. Introduce a convenient quantity of the powdered rock into the bulb and weigh again, so obtaining the weight of the sample. Clamp the tube in a horizontal position and apply the heat of a bunsen burner to the mineral. The water will be driven off and will collect in the bulb, which may be cooled if necessary by applying wet filter paper. When all has been driven over, fuse the tube behind the bulb in which the water has collected and draw the two portions apart. Allow the part containing the water to cool, then weigh it. Heat it again to drive off the water, aspirate the tube till quite dry and weigh again. In this manner the weight of the water is obtained directly. Care must be taken that the outside of the tube is quite clean. The powdered rock is best introduced into the bulb by means of a small thistle-tube, *d*, fine enough to fit into the interior of the Penfield tube and long enough to reach from end to end.



116. Determination of Carbon dioxide

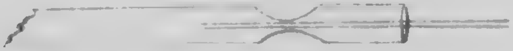
When carbonates are present in a clay carbon dioxide may be determined as described under **88-90**.

---

[1] [illegible] 1894 [illegible]

117. Determination of Ferrous Iron. It frequently happens that, in an iron-bearing clay, a part of the iron is in the ferrous condition. The method for estimating iron already described results in the determination of the total amount present. To ascertain what amount of it is present in the ferrous condition, the following method of procedure should be adopted.

Introduce about 0.5 gram of the very finely ground clay into a tube of resistant glass and draw out its open end somewhat to form a funnel through which acid may be poured. Add a very little water and boil briskly, so that the clay may be freely suspended in the liquid and may hold no air bubbles. Next add diluted sulphuric acid (about 2 parts concentrated acid to 3 parts of water by volume, and which has been previously boiled to free it from air) till the tube is three-fourths filled. Pass in a rapid stream of carbon dioxide (Fig. 1), delivered from a narrow tube made from the same glass as the decomposition tube, so that the subsequent sealing of them together may present no difficulty. While the stream of gas is still passing, heat the narrowest part of the decomposition tube and draw it out till the two tubes fuse together; then stop the stream of gas and rapidly seal off the delivery tube (Fig. 2). When the glass has cooled, place the sealed tube in an oven and heat it [illegible] 200° till the clay does not appear to be further decomposed by longer heating. Allow the tube to cool, open it and rinse the contents into a beaker, dilute largely with water and titrate with a solution of potassium permanganate.[1]



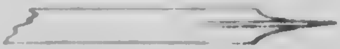


Fig. 2

The foregoing method of displacing air from the tube before sealing is more difficult but much more effective than the one commonly employed, namely, dropping a few small crystals of sodium carbonate into the acid just before the tube is sealed.

HAEMATITE.

Red haematite consists essentially of ferric oxide, while brown haematite is a partly hydrated ferric oxide; there is so little difference in the analytical methods to be employed that they may be considered together. The method of analysis adopted will depend on whether it is required for technical or scientific purposes; the former, being much shorter, will be considered first.

The constituents which it is generally necessary to determine are iron, silica, sulphur and phosphorus.

118. The **general plan of the analysis** is as follows:

(1) Determine the iron by dissolving the ore in hydrochloric acid, reducing the ferric chloride and then titrating either with potassium permanganate in the presence of a "preventive solution" or with potassium bichromate. Should the residue insoluble in acid contain iron it is fused and the iron determined in a similar manner after being brought into solution.

(2) A separate portion is taken for the other determinations. It is dissolved as far as possible in hydrochloric acid containing a little nitric acid, the insoluble part being then fused, treated with hydrochloric acid and mixed with the rest of the solution.

(3) *Silica* is determined by evaporation and dehydration, and weighed by loss after treatment with sulphuric and hydrofluoric acids.

(4) *Phosphorus* is precipitated in the filtrate from the silica in the form of ferric phosphate along with the hydrated oxides of iron and aluminium, and is separated from these as ammonium phosphomolybdate, subsequently being determined by one of a variety of methods.

(5) *Sulphur* is determined in the filtrate from the precipitate produced by ammonia. It is precipitated by barium chloride (being present as sulphates) and weighed as $BaSO_4$.

119. Determination of Iron. The method here described is based on the following reactions: reducing ferric salts to ferrous salts by means of stannous chloride, removing the excess of the latter by precipitation with mercuric chloride, and titrating the ferrous salt with standard potassium bichromate or permanganate (**33**). Under ordinary conditions iron cannot be titrated with the latter in the presence of chlorides but they do not interfere if present in only moderate amount when a mixture containing manganese sulphate and phosphoric acid is previously added. Such a mixture is here known under the name of "preventive solution." This method gives good enough results for technical work if the standardisation of the permanganate and the subsequent titrations are done under exactly the same conditions."

---

[1] This method is not without defects. Errors may arise from (*a*) incomplete decomposition of the clay; (*b*) presence in it of sulphides (pyrites), its oxidation in the presence of the ferric salt and consequent reduction of the latter; (*c*) presence of carbonaceous matter. For a fuller account of this method see *Jour. Amer. Chem. Soc.*, XXII, 1900, p. [illegible]

(2) The following is the result of a (very incomplete) analysis of Chinese Kaolin:— SiO_2 [illegible]%, H_2O 10.01%, Al_2O_3 32.74%, Fe_2O_3 2.64% (total iron), CaO .6%; MgO .27%; K_2O and Na_2O 2.52% (not differentiated).

120. Weigh out about 0.5 gram of finely ground ore into a small beaker, add 15 to 20 c.c. of water and 5 c.c. of concentrated hydrochloric acid; next add 2 c.c. of a solution of stannous chloride, made from 300 grams each of stannous chloride crystals and concentrated hydrochloric acid, heated till the solution is clear and added to a litre of water. Cover the beaker and boil. Should the liquid turn strongly yellow add (a drop at a time) more stannous chloride till the whole is once more colourless; the reaction is complete when the insoluble residue is quite white. Should the ore contain a ferruginous silicate this end cannot be attained; in such case filter the solution, wash completely and set the filter and residue aside to be treated as described in **121**. A colourless residue need not be filtered out. If the solution, which should not exceed 30 c.c. in volume, is not now yellow, add a little potassium permanganate till a yellow colour appears (so avoiding the presence of an unknown excess of stannous chloride), then add stannous chloride, drop by drop, stirring the mixture after each addition, till the yellow colour is once more just discharged; next add, pouring rapidly, 10 c.c. of a saturated solution of mercuric chloride. The formation of a *white* precipitate of mercurous chloride will indicate that so far all has gone well, but should it turn after a minute or two to a dark precipitate of metallic mercury, it will show that the addition of stannous chloride was not made with sufficient care. In such case the only course is to repeat the analysis from the beginning. Next, quickly wash the contents of the small beaker into a large one and dilute to 500 c.c.; add from 8 to 10 c.c. of the "preventive solution"(**) and titrate quickly with a decinormal solution of potassium permanganate, (**33-38**), or of bichromate, (**43**).

121. Treatment of an insoluble ferruginous residue In case that portion of the ore which does not dissolve in hydrochloric acid and stannous chloride is dark in colour, it should, as previously stated, be filtered out. Place the paper, while still moist, in a platinum crucible, and ignite. Add about five times as much "fusion mixture" (*note* [illegible]) as there is silicate to be fused, and heat with a burner for 15 minutes. Cool quickly, place the crucible and contents in a small, well-covered beaker and add concentrated hydrochloric acid till all the carbonates are decomposed. Remove the crucible and wash it well. Boil the contents of the beaker and add a slight excess of ammonia; filter out the precipitate, wash with hot water, and dissolve from the paper with warm dilute hydrochloric acid. The solution so obtained may be added to the soluble portion before final reduction with stannous chloride, or may be independently reduced and titrated in the same manner. It is necessary to precipitate the iron as a hydrated oxide and to redissolve it, in order to avoid the presence of a large excess of alkaline chlorides, which would interfere in obtaining the proper end point of the titration.

122. Determination of Silica Weigh out from 3 to 5 grams of ore into a small covered beaker, add 5 c.c. of water, 5 c.c. of concentrated nitric, and 15 c.c. of concentrated hydrochloric, acids; heat gradually to boiling, and continue to boil as long as any considerable amount of ore seems to dissolve; renew the hydrochloric acid from time to time if necessary. When the action is complete, dilute the solution with its own volume of water, filter, and wash thoroughly. Ignite the filter in a platinum crucible, and fuse the ash with five times its weight of sodium carbonate (or fusion mixture). Dissolve the mass from the crucible with hydrochloric acid, and unite this solution (including the floating particles of silica) with the filtrate first obtained. Evaporate to dryness, using a porcelain vessel, and taking care to spread the pasty substance over as large a surface as possible. Heat in an air-bath for two hours, between 105° and 115°, stirring from time to time with a glass rod in order to granulate the mass. When cool, add 10 c.c. of dilute hydrochloric acid, and enough water to dissolve all the chlorides. Boil for 5 minutes and filter out the silica; wash with hot water mainly, but from time to time pour a few c.c. of dilute hydrochloric acid over the filter, to avoid the formation of basic compounds. The filtrate contains the sulphur and phosphorus, and is used for their determination.

Place the precipitate in a weighed platinum crucible, without previous drying, and ignite, gently at first, then more strongly, and finally ignite with the blowpipe to constant weight. After weighing, treat with sulphuric and hydrofluoric acids and weigh again, as directed in **98**.

[illegible] 33, [illegible]

(**) Made as follows: 16 grams of manganese sulphate dissolved in 175 c.c. of water, and 33 c.c. of phosphoric acid (s.g. 1.7) and 33 c.c. of sulphuric acid (s.g. 1.82) added.

123. Determination of Phosphorus This determination is made in the filtrate from the silica. Boil the filtrate and add ammonia in slight excess, so precipitating aluminium hydroxide, ferric hydroxide, and ferric phosphate. Filter while still hot and wash [illegible] with hot water, stirring the precipitate from time to time with a glass rod to ensure more complete washing. The sulphur will now be in the filtrate so obtained, and in this it is estimated; the phosphorus is contained in the precipitate as ferric phosphate and may be determined gravimetrically as described in **100**, or, more rapidly, by the following [illegible].

124. Treat the precipitate exactly as described in **100** up to the point where the ammonium phospho-molybdate[85] is obtained, redissolved in ammonia and the washings from the filter-paper added to this solution. Next shake the washings round the flask to completely dissolve the precipitate and add 80 c.c. of water and 10 c.c. of concentrated sulphuric acid. Pass through a Jones reductor,[84] washing the flask and reductor with 200 c.c. of water. Take care that in doing this no air is allowed to enter the reductor with the washings, or hydrogen peroxide will be formed and interfere with the titration. After the reduction, the solution will be dark brown to deep olive green. Immediately titrate with a decinormal solution of potassium permanganate without removing the solution from the flask of the reductor. During the titration the liquid becomes successively green, blue, colourless and pink. The latter is of course the end-point. A blank determination should be made on the reductor by running through it a mixture of 180 c.c. of water, 12 c.c. of ammonia (sp. gr. .96) and 10 c.c. of concentrated sulphuric acid, and immediately following with 200 c.c. of wash water.

This method depends on the fact that, when precipitated under the conditions laid down, ammonium phospho-molybdate contains 12 atoms of molybdenum to 1 atom of phosphorus; and further, that molybdic acid, in the presence of zinc and sulphuric acid, is reduced to derivatives of the oxide Mo_2O_3 which are readily oxidised by permanganate to those of MoO_3. 12 atoms of molybdenum thus correspond to 1 atom of phosphorus, and each atom of molybdenum requires 3 times as much oxygen for oxidation as is required for 1 atom of iron.[87] Each atom of phosphorus, therefore, will (indirectly) require $3 \times 12 = 36$ times as much oxygen as 1 atom of iron. So, if 1 c.c. of the standard permanganate is equivalent to x gram Fe, and 56 and 31 are the atomic weights of iron and phosphorus respectively, the phosphorus equivalent, y, of each c.c. of the permanganate will be found from the proportion,

$$36 \times 56 : 31 = x \text{ gram Fe} : y \text{ gram P},$$

$$\therefore y \text{ gram P} = \frac{x \text{ gram Fe} \times 31}{36 \times 56} = .01538 \text{ times the iron}$$

equivalent of the permanganate. In other words, to convert the iron equivalent of the potassium permanganate used for the titration into its phosphorus equivalent, multiply by 0.01538.

The method is very rapid and gives excellent results, but care must be taken to adhere rigidly to the conditions and on no account to interrupt the manipulation from the point at which the ammonium molybdate is added till the washing is complete. Failure to carry this part of the operation through continuously, or to observe the conditions of precipitation, may result in the deposition of molybdic acid with the ammonium phospho-molybdate; this would of course lead to a high result. The solution must also be titrated immediately after reduction and with as little exposure to air as possible.

125. Determination of Sulphur. This determination is made in the filtrate from the precipitate of hydrated ferric oxide and phosphate. Boil the filtrate down to a bulk not exceeding 300 c.c. Should ammonium chloride crystallise from the liquid, it may be destroyed by adding from 2 to 3 c.c. of concentrated nitric acid, and continuing the heating. Filter the solution, unless perfectly clear; then acidify slightly with hydrochloric acid, bring to a full boil, add 20 c.c. of a 10% solution of barium chloride, continue to boil for 15 minutes, allow to stand (well covered to guard from dust) till cold, filter through a small paper, wash with hot water till the washings are free from chlorides, transfer the moist filter to a weighed crucible, and ignite. To the cool contents of the crucible add two or three drops of dilute sulphuric acid (to reconvert any barium sulphide to sulphate), evaporate, ignite again, and weigh.

---

(84) *Jour. Amer. Chem. Soc.*, 189[illegible], XVIII, [illegible].

(85) $3(NH_4)_2O \cdot P_2O_5 \cdot 24MoO_3$ [illegible]

(86) See Note 7[illegible].

(87) Mo_2O_3 to become MoO_3 requires 3 atoms of oxygen, and $2FeO$ to become Fe_2O_3 requires 1 atom of oxygen.

126. [illegible] ***complete analysis.*** [illegible]

[illegible]

127. The ***general plan of a complete analysis*** [illegible] ***120, 121,*** or by titration with standard potassium bichromate ***44 45 46*** [illegible] ***119-121***

[illegible] ***123***

[illegible] ***96*** [illegible] ***97***

(4) In a fourth portion determine the *water* ***134***

128. Determination of Silica [illegible] by fusion exactly as directed for the technical analysis ***122*** [illegible] through a small [illegible] portion of the silica. A[illegible] very thoroughly as before. The separation of silica [illegible] ride. Dissolve [illegible] and add this solution to the filtrate. See also ***98***

129. Determination of Phosphorus This determination [illegible] the methods given for the technical analysis of the ore. [illegible] work is not essential to use the gravimetric method. In the [illegible] the ammonium phosphomolybdate exactly as [illegible] filtrate and washings, however, should be further tested by [illegible] with 100 c.c. of the solution of ammonium molybdate and ad[illegible] The precipitate is then treated as described [illegible] ***100***

130. Determination of Sulphur The same method [illegible]

131. Determination of Aluminium Weigh out [illegible] washed, be ignited and then driven off as silicon tetrafluoride, a check [illegible] first determination. Any residue from the driven off silica [illegible] and added to the filtrate.

To this filtrate add a solution of sodium carbonate, till the precipitate [illegible] each drop of the alkaline solution falls into the solution of chlorides just [illegible] stirring vigorously. Should the proper point be passed, and a *permanent* precipitate [illegible] formed, reverse the process, adding dilute hydrochloric acid till the precipitate once more [illegible] dissolved. The lution is now neutral and should be clear and deep brown (not yellow) in colour. Next add [illegible] grams of solid ammonium acetate for every gram of iron present. If this operation has been properly carried out, the solution will be still clear, but deeper and redder in colour. Dilute the solution with water to 500 or 1000 c.c., and heat to boiling (it is at this stage that the precipitate appears), allow to boil for from 1 to 2 minutes only, then filter through a large ribbed paper. *Keep the solution hot till the moment it is poured upon the filter.* Wash with boiling water [illegible]. The precipitate consists of the basic acetates of iron and aluminium, with ferric phosphate and adherent manganese, calcium and magnesium salts. To free it from the three latter metals dissolve it in warm dilute hydrochloric acid, neutralise the solution and reprecipitate the basic acetates by the addition of ammonium acetate, dilution and boiling exactly as before. The whole of the manganese, calcium and magnesium will now be in the two filtrates, which should be combined. Owing to the large amount of adhering sodium salts, the basic acetates cannot be ignited directly as oxides. Redissolve the precipitate in warm dilute hydrochloric acid, add a slight excess of ammonia, boil for a few minutes, filter, and wash with hot water. The precipitate consists of ferric hydroxide, aluminium hydroxide, and ferric phosphate. Dry the precipitate, separate it from the paper and place in a small watch glass; place the paper in a weighed crucible and ignite gently. Cool and add the precipitate, again ignite, using the blowpipe till a constant weight is obtained. The iron and phosphorus having already been determined and calculated respectively to Fe_2O_3 and P_2O_5, the weight of Al_2O_3 is obtained by difference, since, for purposes of calculation, $FePO_4$ may be considered as $Fe_2O_3.P_2O_5$.

132. Determination of Manganese Combine the two filtrates from the basic acetate separation and concentrate them to about 500 c.c. Add 10 c.c. of 50% acetic acid and 5 c.c. of bromine and warm on the water-bath (under a good hood). Manganese is precipitated in the form of a hydrated dioxide. When all excess of bromine is expelled, filter the hot liquid, leaving as much precipitate as possible in the beaker, and wash with hot water. Calcium and magnesium are now in the filtrate, but the manganese cannot be advantageously ignited in its present form. Dissolve the precipitate from the beaker and the paper with dilute hydrochloric acid to which a few c.c. of sulphurous acid have been added; wash the solution into a porcelain casserole, make slightly alkaline with ammonia and add sodium hydrogen phosphate solution in slight excess; next add hydrochloric acid till the precipitate redissolves, warm the solution and add once more ammonia in very slight excess. Stir the solution and boil for a minute, then place it on the water-bath, and allow it to digest till the amorphous precipitate, which was at first formed, has become wholly crystalline. Filter, and wash with water. The precipitate is manganese ammonium phosphate ($NH_4MnPO_4.H_2O$). Dry the filter, separate the precipitate and filter-paper; burn the latter in a *porcelain* crucible, add the precipitate to it and ignite strongly. Weigh as manganese pyrophosphate ($Mn_2P_2O_7$).

133. Determination of Calcium and Magnesium These metals are found in the filtrate from the hydrated manganese dioxide, and are separated and determined by exactly the same method as is indicated under the analysis of Limestone, **96** and **97**.

134. Determination of Water. This should be done as described in **115**.

The subjoined analyses may be of interest:

Locality.	Jackson Mine: Lake Superior.	Negaunee Manganiferous Haematite.
Fe_2O_3	93.75	65.40
MnO	trace	6.71
Al_2O_3	0.73	1.46
CaO	0.61	0.45
MgO	0.23	0.66
Sulphur	0.03	0.04
P_2O_5	0.32	0.16
Water and organic matter	1.09	2.46
SiO_2	3.27	22.67
	100.03	100.01

COAL.

135. The analysis of a coal for technical purposes generally includes the following determinations: *moisture, volatile combustible matter, fixed carbon, ash* and *sulphur*. As the results obtained in the determination of the first three of these cannot be considered as representing any definite constituents of the coal, a variation in the method of analysis will almost invariably cause the results to vary somewhat. In order for the proper interpretation of these results it is necessary that the methods employed be fixed and not diverged from. In spite of their indefiniteness the results are of importance in judging the quality of a coal. Determinations of ash and sulphur are of course definite and the results obtained by different methods on the same sample of coal necessarily agree, as the determinations of chlorine in a sample of common salt. The term "sulphur" is, however, intended to include only that portion present in the form of sulphides and not that which is almost always present as a sulphate. The amount of the latter has [illegible] technical significance.

136. Determination of Moisture. From 1 to 2 grams of the sample are weighed into a porcelain or platinum crucible or basin and dried for 1 hour in a hot air bath, the temperature of which is kept between 104° and 107°. At the end of this time it is weighed again and the loss of weight considered as moisture.

137. Determination of Ash. The portion used for the moisture determination is here employed. Place the crucible, which has been placed on its side, and ignite, carefully at first, till all gases are off, then more strongly, stirring from time to time with a stout platinum wire to expose a fresh surface to the air and so keep up the combustion. When completely ignited the ash will be light gray or brown and must be constant in weight. The weight of the residue gives the amount of ash directly.

138. Determination of Volatile Combustible Matter. Weigh about 1 gram of coal into a platinum crucible of medium size (20 to 30 grams), cover closely, place on a triangle (which is made of platinum wire) and ignite, carefully avoiding draughts, for *exactly seven minutes* with the full flame of a Bunsen burner. So adjust the crucible that its bottom is about 8 cm. above the top of the burner, the length of the flame being at least 20 cm. At the end of the seven minutes, by which time there should be no signs of combustible gases being evolved, cool the crucible and contents, wipe away any soot deposited on the *outside* of the crucible or lid and weigh. The loss of weight represents the volatile combustible matter plus the moisture plus half of the sulphur present as sulphides.

139. Determination of Fixed Carbon. This is found by difference. The weight of material left in the crucible after the determination of volatile combustible matter represents the fixed carbon plus the ash plus half the sulphur present as sulphides.

140. Determination of Sulphur. This is most usually made by some modification of Eschka's method; the following is convenient and works well.

Mix from 1 to 2 grams of finely powdered coal with 1 gram of magnesium oxide and 0.5 gram of anhydrous sodium carbonate. Place the mixture in a large platinum crucible, turn it on its side and heat gently, taking care not to fuse the contents, and stirring occasionally with a platinum wire. Continue the heating till the carbon of the coal is entirely oxidised. Allow the crucible to cool, transfer its contents to a beaker, add about 150 c.c. of water and boil for about 10 minutes. Filter and wash the residue on the filter (it consists of unchanged magnesium oxide and the insoluble part of the ash) with hot water. To the filtrate add 15 c.c. of bromine water, boil for 5 minutes, acidify with hydrochloric acid, and continue the boiling till all bromine is expelled. Then add 10 c.c. of a boiling solution of barium chloride, continue the boiling for another 5 minutes, allow the barium sulphate to settle, filter and wash this precipitate with hot water till free from chlorides and treat it as described in **82**. Its weight is then calculated to sulphur.

In the above determination special care must be taken to use magnesium oxide as free as possible from sulphur. It is difficult to find a sample containing none, so a determination of the amount present should be made on a sample of about 20 grams and a suitable correction introduced in calculating the results of an analysis.

When particular exactitude is desired, the acidified solution should be evaporated to dryness and the small amount of silica dehydrated as described in **98**. The salts are then redissolved in water, the solution filtered and the analysis continued as before. An alcohol lamp should also be used instead of a bunsen burner during the combustion as coal gas is never quite free from sulphur compounds, the products of combustion of which may be absorbed by the alkali.

141. Calculation of results The following results were obtained on a sample of bituminous coal:

Loss on drying at 105 – 107° for 1 hour (moisture)	[illegible]
Loss on igniting for 7 minutes (moisture + volatile combustible matter + ½ sulphur)	[illegible]
Ash	[illegible]
Sulphur	[illegible]

The amount of volatile combustible matter was therefore,

$$[illegible] - [illegible] - \frac{1.41[illegible]}{2} = [illegible]$$

The results of the analysis would be reported as follows:

Moisture	[illegible]
Volatile combustible matter	[illegible]
Ash	[illegible]
Sulphur	[illegible]
Fixed carbon (by difference).	[illegible]
	100.00

141a. While the composition of a coal conveys much useful information in regard to its nature, there are other properties of which the numerical analytical results give little indication. In the case of bituminous or soft coals their **coking qualities,** the property possessed by them of forming caked masses of coke when subjected to destructive distillation, are of importance. The best coking coals give about 65% of coke, and such coals are consequently very valuable for metallurgical processes. In making the determination of the "volatile combustible matter" (**138**), the hardness and compactness—or the reverse—of the residue left in the crucible should be observed and noted.

Important also to the user is the **Calorific Value** of a fuel. To express such a factor numerically a standard unit of heat is required, and the one employed is the calorie. This is the amount of heat required to raise the temperature of 1 gram of water through 1° C. (best between the limits of 0° and 40° C.). [illegible] Employing this unit the "*Calorific Value*" *is the number of grams, kilograms, or pounds of water which 1 gram, kilogram or pound of the fuel can raise through 1° C.* Results of calorimetric determinations are often given in British Thermal Units, a B.T.U. being the number of pounds of water that can be raised through 1° Fah. by the combustion of 1 pound of the substance burned. The latter will evidently be [illegible] of the former, as 1° C. is equivalent to [illegible]° on the Fahrenheit scale.

For example, if the heat evolved by the combustion of 1 gram of a coal were completely absorbed by 1000 grams of water, and in the process raised the temperature of the water through 8° C., then 8000 calories would have been evolved, and the "Calorific Value" of this coal would be stated to be 8000. That is to say, 8000 grams of water could be heated 1° C. by 1 gram of the coal; and, equally, 8000 *pounds* of water could be heated 1° by 1 *pound* of the coal. (This in B.T.U's. would be [illegible] × 8000). Now it has been found that in order to convert 1 gram of water at 100° C. into vapour at 100° C., 537 calories are required; this number, 537, is known as the "latent heat of steam." Hence the "Evaporative Power" of the coal taken as an example would be $\frac{8000}{537} = 14.9$. That is, the number of grams, kilograms, or pounds of water which 1 gram, kilogram, or pound of it could convert into vapour.

Numerous forms of calorimeters are employed for ascertaining the heat-producing qualities of a coal, but either defects and inaccuracies pertain to the use of the simpler forms or the difficulties in manipulating the high-pressure bomb instruments forbid their general use. A calorimeter which seems to combine simplicity with accuracy is that of S. W. Parr. [illegible] It is based on the principle of causing the coal to undergo combustion in contact with sodium peroxide, which besides supplying the oxygen required, is capable of absorbing the products of combustion, thus avoiding the liberation of these gases on the one hand or their retention under high pressure on the other. The following description of the apparatus is taken from the original paper.

[illegible]

[illegible] Amer. Chem. Soc. XXII [illegible]

[illegible]

D

[illegible]

K
B
A
G
C
E
D

[illegible]

The number of *pounds* of this coal required to evaporate 1000 *pounds* of water, starting from 10° C., would be the same, for, in order to express in B.T.U.'s the heat required and the "calories" which the coal is capable of evolving, the numbers given above must each be multiplied by the ratio; this leaves the fraction $\frac{627000}{8000}$ unchanged. The number of *pounds* of the coal required for 1000 *pounds* of water is thus equal to the number of *grams* necessary to effect the same change in 1000 *grams* of water.

The problem might also be worked in B.T.U.'s at once. To raise 1 pound of water through 180° Fah. requires 180 B.T.U.'s.

Therefore to raise 1 pound from 10° C. (= 50° F.) to 212° F. requires 162 B.T.U.'s.

The latent heat of steam is 537 × 1.8 = 966.6 B.T.U.;

∴ the total heat required for 1 pound of the water = 1128.6 B.T.U.'s

and ∴ 1000 pounds require 1128600 B.T.U.'s

But the coal has a calorific value of 8000 × 1.8 = 14400 B.T.U.'s

∴ the amount of coal required would be $\frac{1128600}{14400}$ = 78.3 pounds.

COPPER MATTE.

This substance, formed during the smelting of copper, is a mixture of the sulphides and oxides of copper and iron, but commonly contains also considerable amounts of lead, zinc, and arsenic.

142. For technical purposes it is seldom necessary to determine any constituent but the copper. The electrolytic method is almost universally adopted, and may be carried out as follows.

Dissolve about 0.5 gram of matte in 10 c.c. of dilute and 5 c.c. of concentrated nitric acid: a gentle heat will be sufficient to complete the solution. Evaporate to about half the original volume then add 20 c.c. of water. Filter out the insoluble matter and wash thoroughly with hot water. Run the filtrate and washings into a weighed platinum dish: add ammonia till the solution is almost but not quite neutral and then add 2 c.c. of concentrated sulphuric acid. Electrolyse the solution, after diluting to a convenient bulk, making the dish the kathode. The conditions under which electrolysis is best carried out are, voltage 2-3, current 0.8-1 amperes for every 100 sq. cm. of cathode surface;[illegible] time, 0.2 gm. of copper will be deposited in about 1 hr. Complete precipitation may be insured by testing a few c.c. of liquid with hydrogen sulphide.[illegible] When it is seen that no more copper is present in the solution, syphon off the liquid, replacing it by hot water as rapidly as it is removed; next interrupt the current, pour off the water, wash the dish with a little alcohol, dry at 100° and weigh. Sometimes the solution to be electrolysed is placed in a beaker, the kathode being a suspended cone or cylinder of stout platinum foil. When this arrangement is used it is not necessary to filter the solution before electrolysis, since the insoluble matter settles to the bottom of the beaker and not on the kathode. The vessel in which the electrolysis is carried out should be covered by two slips of glass, fitting against the anode wire. The lower surface of these glasses will become covered with little droplets of the solution, carried up mechanically by bubbles of gas, and should be washed down from time to time.

143. For a **complete analysis** it is best to use two portions, one for the determination of the metals, the other for the determination of sulphur. For the former a convenient scheme is as follows:

(1) Dissolve in nitric acid as completely as possible, then evaporate with hydrochloric acid and filter out the *siliceous residue*, which will probably carry traces of lead sulphate: the latter is removed by washing with a solution of ammonium acetate and the recovered lead is added to the previous filtrate.

(2) In the filtrate from this residue precipitate *copper*, *arsenic* and *lead* as sulphides. These should be reprecipitated to remove the trace of zinc which may have been carried down. They should then be separated as detailed in the sequel, being weighed separately as copper, magnesium pyro-arsenate and lead sulphate.

[illegible]

[illegible]

[illegible] the filtrate [illegible] precipitated as the basic acetate [illegible]

[illegible] In the filtrate from the iron, *zinc* may be precipitated as the sulphide and weighed as oxide, [illegible] metallic zinc after [illegible]

[illegible] In another portion, *sulphur* is determined and weighed as barium sulphate. Any lead [illegible] in the insoluble residue is determined and calculated to sulphur.

144. The sample should not be too finely ground or it will be difficult to decompose. Dissolve about 0.5 gram of the copper matte in 10 c.c. of dilute and 5 c.c. of concentrated nitric acid. Apply heat only very cautiously at first. When the solution is almost complete add 10 c.c. of concentrated hydrochloric acid and evaporate to dryness. Take up with 5 c.c. of dilute hydro[illegible] sufficient water to complete the solution. Filter out the insoluble matter and [illegible]

145. Determination of gangue. The insoluble matter consists of gangue with [illegible] traces of lead sulphate. Pour over the filter [illegible] c.c. of a concentrated solution of [illegible] acetate, then wash with warm water and add these washings to the [illegible] previously obtained. Burn the moist filter paper and weigh the gangue in a porcelain crucible.

146. Separation of copper, lead and arsenic from iron and zinc. Dilute [illegible] Warm till nearly boiling, add 5 c.c. of dilute hydrochloric acid and pass in hydrogen sulphide till no more precipitate forms. Filter while still hot and wash with water saturated with hydrogen sulphide. Again test the filtrate with more hydrogen sulphide, to ensure the complete precipitation of arsenic. The precipitate is liable to carry down traces of zinc, [illegible] before freeing it from these it is best to separate the arsenious sulphide. For this purpose, [illegible] the precipitate, on the paper, with 20 c.c. of a strong solution of sodium sulphide, then wash with water. Put aside the filtrates and washings, which contain arsenic as sodium thioarsenite, to be treated as described in **147**. Dissolve the mixed sulphides through the paper in hot dilute nitric acid, wash with hot water, dilute largely, warm and pass hydrogen sulphide till no further precipitate forms. Filter through the same paper and wash as before: the precipitate [illegible] of lead and copper sulphides, **148** and **149,** and the united filtrates contain all the iron and zinc, **150, 151.**

147. Determination of Arsenic. This is present in the solution obtained by treating the mixed sulphides with sodium sulphide. To the solution add dilute hydrochloric acid, very cautiously, till the liquid is faintly acid. Filter out the precipitate of arsenic trisulphide and sulphur. Dissolve the arsenic trisulphide from the paper by treatment with about 20 c.c. of [illegible] and wash the paper with hot water. To the ammoniacal solution add an excess of nitric acid, then about 0.2 grams of potassium chlorate. Boil to complete the oxidation and expel all chlorine. Next neutralise with ammonia and add a slight excess of "magnesia mixture." Stir the solution well, and allow to stand for at least six hours. Filter through a *small* paper and wash the precipitate of magnesium ammonium arsenate with dilute ammonia. When the washing is complete, dissolve the precipitate from the paper by the use of a few drops of dilute nitric acid. Wash the paper thoroughly with hot water and allow the solution and washings to run into a weighed porcelain crucible. Evaporate to dryness and ignite. Weigh the arsenic as magnesium pyro-arsenate ($Mg_2As_2O_7$). (The precipitate is dissolved from the paper, and not burned directly, in order that there may be no chance of reduction, and consequent loss of [illegible] arsenic.)

148. Determination of Lead. Re-dissolve the mixed sulphides of lead and copper in hot dilute nitric acid. Place the solution in a porcelain vessel, add 10 to 15 c.c. of concentrated sulphuric acid, and evaporate on a sand-bath or hot-plate till heavy white fumes of sulphur trioxide are evolved. Cool the acid [illegible] and add about 50 c.c. of water and 50 c.c. of 95 [illegible] for a few minutes, then filter and wash with dilute alcohol till all the copper is removed. [illegible] **83**

149. Determination of Copper. The filtrate from the lead sulphate should be evap[illegible] neutralise the resulting solution by means of ammonia, and [illegible] conditions as to current, etc., that were given in **142**

In cases where there are no facilities for determining copper electrolytically, it is best to re[illegible] it as the sulphide, then ignite the precipitate strongly in a porcelain crucible. Cool and add a few drops of nitric acid, evaporate cautiously and re-ignite (using a bunsen burner only). Weigh the copper as cupric oxide.

150. Determination of Iron. The filtrate from the sulphides of lead and copper contains iron and zinc. Boil this solution and add a few drops of nitric acid (or better, a few c.c. of bromine water) to completely re-oxidise the iron to the ferric condition. Filter out any sulphur that may separate, make the solution almost neutral and precipitate the iron as the basic acetate in the manner described in ***131***. The filtrate will contain the greater part of the zinc, but some will be retained by the basic ferric acetate. Dissolve the latter in hot dilute hydrochloric acid, boil the solution, and add a slight excess of ammonia; filter and wash with hot water. Dry the precipitate and separate it from the paper before igniting the latter. Finally ignite the whole and weigh as ferric oxide.

151. Determination of Zinc. This is contained in the two filtrates from the iron. Evaporate them together to a convenient bulk. Make the solution alkaline, and while warm pass in hydrogen sulphide (should any quantity of manganese, nickel or cobalt be present they will be readily detected by the discolouration of the white zinc sulphide, and suitable means may be taken for separating them. For such means larger works should be consulted) till the liquid is saturated. Allow the precipitate to subside. If no more forms in the supernatant fluid when more hydrogen sulphide is passed, the precipitation is complete. Filter and wash the precipitate with water containing a little ammonium sulphide and ammonium nitrate. Dissolve the zinc sulphide from the filter by means of warm dilute sulphuric acid. Collect the solution in a weighed platinum dish (*). Add 1 gram of sodium acetate and 0.3 c.c. of acetic acid. Dilute to 150 c.c., warm to 65°C., and keep the liquid at this temperature while it is being electrolysed. Use a current of 0.36 ampère for 100 sq. cm. of cathode surface and an e.m.f. of 4 volts. At the end of about an hour the liquid will appear to be filled with bubbles. At this point, neutralise the liquid by adding a few drops of dilute ammonia, raise the current to about 0.7 ampere (5 volts) and continue the electrolysis. When a test shews that all the zinc has been removed, syphon off the solution, wash with alcohol, and finally with a little ether. Dry the deposit by holding the dish for a moment in the hand. Weigh as metallic zinc.

152. When it is known that no nickel is present in the filtrate from the iron (it is of very rare occurrence), precipitation of zinc sulphide may be entirely omitted, and the electrolysis proceeded with directly. About 0.1 gram of zinc is deposited per hour under these conditions, on a cathode surface of 100 sq. cm.

Zinc should never be electrolytically deposited directly upon platinum, as it leaves a spongy surface when redissolved. A platinum dish to be used for this purpose is readily prepared by depositing upon it a thin electrolytic coating of silver. A silver dish may be used as the kathode if it is conveniently at hand. When the electrolytic method is not available, the following course of procedure may be followed: precipitate and wash the zinc sulphide as already described and dissolve from the paper with dilute hydrochloric acid. Wash the solution into a porcelain casserole and add a slight excess of a recently prepared solution of sodium carbonate. Boil for 5 minutes, filter and wash with hot water till the precipitate is free from alkali. Dry the precipitate, separate it from the paper, ignite the latter in a porcelain crucible, add the precipitate to the ash and ignite strongly. Weigh the zinc oxide. This method, however, is not a desirable one.

153. Determination of Sulphur. Weigh out 0.5 gram of matte, add 20 c.c. of dilute nitric acid and heat very cautiously. After the first reaction has subsided add about 0.5 gram of potassium chlorate dissolved in cold concentrated nitric acid and continue to heat cautiously till all the sulphur has dissolved. Care must be taken not to raise the temperature too rapidly or part of the sulphur may fuse into globules which it will be almost impossible to oxidise. Evaporate with hydrochloric acid to expel nitric acid, then dilute the solution, filter out and wash the gangue. Preserve the latter for further examination, (***154***). Boil the filtrate, and add a slight excess of dilute ammonia; filter out the precipitate of ferric hydroxide, and wash with hot water. Boil the filtrate to expel the excess of ammonia. Acidify slightly with dilute hydrochloric acid, and while boiling add a slight excess of a solution of barium chloride. Allow the precipitate to settle, while standing in a warm place, filter and wash, by decantation at first, with hot water. Ignite precipitate and paper together in a weighed crucible; cool, add a few drops of dilute nitric acid and a drop of concentrated sulphuric acid (to convert any barium sulphide into sulphate), evaporate gently, ignite when dry, weigh the barium sulphate and calculate to sulphur.

(*) See *Jour. Amer. Chem. Soc.* 1902 XXIV 105.

(**) A convenient alternative method of dissolving copper matte is to warm the powdered substance gently with 15 c.c. of concentrated nitric acid and 2 or 3 c.c. of bromine. The method applies equally well to the solution of natural sulphides (See ***156***). Its especial merit is that there is less danger of the sulphur forming insoluble beads. *Jour. Amer. Chem. Soc.* XXII 1900 102.

154. The gangue may be contaminated with lead sulphate and the sulphur present in this [illegible] ammonium acetate (which will dissolve out any lead sulphate) and wash with hot water. To the filtrate add 5 c.c. of acetic acid and a slight excess of a solution of potassium chromate. Filter any lead chromate which may be precipitated through balanced filter papers. Wash with hot water, dry at 110°, weigh, and calculate the weight of sulphur to which [illegible]

PYRITES

The simplest member of this class of minerals is iron pyrites, FeS_2. Many metals, notably copper and nickel, may replace the iron, wholly or in part, while sulphur may be replaced by arsenic and occasionally by antimony. Gold is also found in many samples of pyrites. For technical purposes it is usually sufficient to determine copper and nickel.

155. The ***general plan of analysis*** is as follows:- Both copper and nickel are determined electrolytically in the same portion of mineral. The former is deposited from a solution containing nitric and sulphuric acids. The latter is deposited from a solution of its sulphate, containing ammonia and ammonium sulphate.

156. Dissolve 1 gram of moderately ground pyrites, by pouring over it dilute nitric acid and gently heating on a water-bath [illegible]. After the reaction has proceeded for some time, add 10 c.c. of concentrated nitric acid, and raise the temperature, by bringing the water in the bath to the boil. Should the mineral not wholly dissolve, it may be boiled on a hot plate (or sand bath), concentrated nitric acid being added from time to time as required.

157. *Determination of Copper* Cool the solution and add 10 c.c. of concentrated sulphuric acid; evaporate till all the nitric acid is expelled and heavy sulphurous fumes are evolved. Cool the solution, dilute to 50 c.c. by the cautious addition of water, and filter out the gangue (if cylinder electrodes are to be employed later, the filtration may be omitted). Wash the filter paper well, and add to the filtrate enough ammonia to produce a *faint* precipitate of ferric hydroxide; add 1 c.c. of dilute sulphuric acid. Transfer the solution to a platinum dish, and electrolyse, observing the conditions laid down for the deposition of copper in **142**.

158. *Determination of Nickel* The solution from which the copper has been deposited is used for this determination. Transfer it with the washings to a beaker, raise the temperature almost to boiling and precipitate the iron by adding a slight excess of ammonia, after ensuring the complete oxidation of the iron by adding a few c.c. of bromine water. Filter out the ferric hydroxide, which carries down with it some nickel. Wash it with hot water, then dissolve it from the filter paper by pouring over it warm dilute sulphuric acid. Re-precipitate the iron by means of ammonia and add this filtrate to the first. Again re-dissolve the iron and re-precipitate it, adding the filtrate to the first two.

Evaporate the filtrates, after adding a slight excess of sulphuric acid, till sulphurous fumes are evolved (this precaution is taken in order to drive off any nitric acid which may have escaped reduction during the deposition of the copper). Cool the solution, dilute to a convenient volume with water, add 5 grams of ammonium sulphate, neutralise with ammonia and add 30 c.c. of the latter in excess of what is required for that purpose. Transfer the solution to a weighed platinum [illegible] volts, and a current of 0.5 to 1.5 amperes for each 100 sq. cm. of kathode surface [illegible]. The best deposit is generally obtained at the ordinary temperature, but quicker results follow by heating the liquid to 50°. Under the former conditions, a current of 1.5 amperes deposits 1 gram of nickel in about 2 hours; at 50° the deposition is [illegible] half the time. During electrolysis the dish must be covered by glass slips [illegible] must be washed down from time to time. The reaction is [illegible] place in contact with a drop of ammonium sulphide. When this point is reached, syphon off the [illegible] replacing it with hot water. Finally, interrupt the current, pour off the water, wash the [illegible] alcohol, dry at 100° and weigh. The deposit of nickel should be hard, [illegible]

[illegible]

159. An excellent **separation of iron and nickel** may be effected as follows. To the solution from which the copper has been electrolytically deposited add a few c.c. of bromine water, heat almost to boiling and add an excess of ammonia. Filter out the iron precipitate which carries with it some nickel. Dissolve the precipitate in hot dilute hydrochloric acid and evaporate till pasty. Add 10 c.c. of hydrochloric acid (sp. gr. 1.1) and transfer the solution to a separating funnel. Extract the ferric chloride by means of ether, as described in **168**. The aqueous layer will contain all the nickel carried down by the ferric hydroxide. Add it to the filtrate from the latter, warm gently to expel the ether, then acidify with sulphuric acid and evaporate till sulphurous fumes are evolved; proceed with the determination of nickel as described in the previous paragraph.

160. A more **complete analysis** involves the determination of the following constituents: sulphur, arsenic, antimony, copper, lead, iron and nickel.

161. The **plan of analysis** is as follows:

(1) Dissolve a portion of the mineral and determine the sulphur (weighing it as barium sulphate) as described in **153** and **154**.

(2) In a separate portion determine the other elements. Dissolve as before and, after filtering out gangue, precipitate arsenic, antimony, copper and lead by means of hydrogen sulphide. Arsenic and antimony should be separated from copper and lead by the use of a solution of sodium sulphide as described under the separation of arsenic alone from those metals in **146**.

(3) Separate arsenic and antimony from one another by oxidising the solution of sodium thioarsenite and sodium thioantimonite by means of aqua regia. Precipitate arsenic as magnesium ammonium arsenate and, in the filtrate, determine antimony by the method described later.

(4) Separate nickel and iron by the repeated re-precipitation of the latter, as described under the technical analysis of this mineral (**158**). Determine the nickel electrolytically, as there described, and determine iron by weighing as ferric oxide. As an alternative, the iron and nickel may be separated by the ether extraction method (**168**) and the nickel determined as before. Iron may then be determined in a separate portion of the mineral, after separation from the nickel by three precipitations with ammonia, and weighed, after ignition, as ferric oxide.

162. The only point calling for more full description is the **determination of arsenic and antimony.**

Dissolve the mineral as already described (**156**) in nitric acid, evaporate twice with concentrated hydrochloric acid, dissolve in water, filter out the gangue and pass hydrogen sulphide into the filtrate (which should be meanwhile heated) till precipitation is complete. Filter out the precipitate, which may consist of copper, lead, arsenic and antimony sulphides, and wash with water containing hydrogen sulphide. Arsenic and antimony sulphides will in this way pass into solution, while copper and lead sulphides remain unacted upon.

163. Separation of Arsenic and Antimony. Dilute the solution to 50 or [illegible] c.c. and acidify with dilute hydrochloric acid; add aqua regia, and warm gently at first, but more strongly later, till the re-precipitated sulphides are entirely dissolved. Filter out any sulphur which may remain unoxidised, and wash with hot water. Cool the filtrate and make it faintly alkaline with ammonia. Add 20 c.c. of "magnesia mixture" (*note* [89]), stir thoroughly and allow the whole to stand for 12 hours. Filter out the precipitate of magnesium ammonium arsenate and wash it with dilute ammonia; antimony will remain in the filtrate. Re-dissolve the precipitate of magnesium ammonium arsenate in a little hydrochloric acid (washing the paper thoroughly with of water), cool the filtrate, and re-precipitate by making strongly alkaline with ammonia. Allow 12 hours again for the re-precipitation and treat the precipitate as described in **84**.

164. Determination of Antimony. Acidify the filtrate from magnesium ammonium arsenate with hydrochloric acid; almost boil the solution and at the same time pass into it a rapid stream of hydrogen sulphide. Filter the precipitate of antimony sulphide and wash it with a solution of hydrogen sulphide. Dissolve the precipitate by pouring over it about 25 c.c. of a *saturated* solution of sodium sulphide (made from the pure crystallised salt), and wash the filter paper with hot water. Catch the solution in a weighed platinum dish,[90] add a further 25 c.c. of a 20% solution of sodium sulphide and make up to a convenient volume with water. Warm the solution to about 70° and maintain it at this temperature while it is electrolysed. The current for [illegible] per sq. cm. kathode surface should be 1 to 1.5 amperes; e.m.f. 2 to 3 volts.[illegible] The dish must be closely covered to prevent loss by evaporation or spattering. When the electrolysis is complete, syphon off the solution, at the same time replacing it with a stream of distilled water. Interrupt the current, finally wash the deposit with alcohol and ether and dry by the heat of the hand. Weigh the dish [illegible] deposit of antimony.

---

[89] *Jour. Amer. Chem. Soc.*, XXI (1899) p. [illegible]

[90] [illegible] *M*[illegible] Eng. [illegible] 1898 p. 140.

165. W[illegible] a volumetric method may be used, [illegible]

Dissolve [illegible] sodium hydroxide. Add an excess of hydro[illegible] acid and successive small portions of potassium chlorate. Boil the solution down to [illegible] c.c. volume,[illegible] taking care that there is still some excess of hydrochloric acid present, in order that all the chlorate may be decomposed; cool the solution, add 15 c.c. of [illegible] hydrochloric acid, and make up the solution to a volume of about 700 c.c.; add 3 or 4 grams of potassium iodide (free from iodate), and titrate immediately with a decinormal [illegible]

The reaction may be represented by the following equation: $SbCl_5 + 5KI = SbI_3 + 5KCl$ [illegible]

166. Another method of estimating the antimony is to re-precipitate in the filtrate from the magnesium ammonium arsenate precipitate (**163**) by adding hydrochloric acid and passing hydrogen sulphide. The precipitated sulphide is treated with nitric acid, dried, ignited and weighed as Sb_2O_4.

NICKEL-STEEL.

167. ***Determination of Nickel in Nickel-Steel.*** The following method has been extensively used for the separation of nickel from iron.[illegible] It is also applicable where iron [illegible] separated from copper, manganese, uranium [illegible] and zinc.[illegible] It is, unfortunately, only applicable where the metals are present in the form of chlorides and depends on the solubility of ferric chloride in ether containing hydrochloric acid. Its superiority to any method whereby iron must be precipitated and re-precipitated is at once obvious. The separation is also very clean and [illegible]. The exact manipulative details vary somewhat according to the metals present. For instance, it is necessary to make three extractions to completely separate iron from uranium.

168. The method of separation, which was referred to in **159**, is as follows:

Weigh out 2 grams of nickel-steel into a porcelain dish or casserole provided with a good [illegible]. Dissolve the steel in dilute hydrochloric acid, with the aid of heat. Add 1 c.c. of concentrated nitric acid, to oxidise ferrous to ferric chloride, and evaporate the solution to complete dryness. Dissolve the mass in 20 c.c. of dilute hydrochloric acid and evaporate again to a bulk of [illegible] transfer to a separating funnel of about 250 c.c. capacity, washing the dish with the smallest possible quantity of dilute hydrochloric acid. Cool the solution thoroughly and add 40 c.c. of ether, which must be free from alcohol and must have been just previously shaken [illegible] in 60 c.c. of dilute hydrochloric acid. Shake vigorously for 10 minutes, cooling the contents of [illegible] from time to time. Separate the aqueous from the ethereal layer, washing the latter (which now contains all the iron) twice with from 5 to 10 c.c. of dilute hydrochloric acid. Gently warm the aqueous layer to expel ether and proceed with the determination of nickel by the usual methods, **158**. Sometimes a second or third extraction with ether is necessary to completely separate all iron.

ANALYSIS OF IRON.

169. As commercially known, iron and steel contain, as accessory constituents, carbon, sulphur, phosphorus, and silicon, the accurate determination of all of which is very important for technical purposes. Other metals are also often present; most pig-iron contains a small quantity of manganese, (**181**), nickel-steel is commonly met with in commerce (**167, 168**), and steels are now being used which contain molybdenum, tungsten, uranium and other metals; titanium [illegible] frequently contained in pig-irons. The methods employed in determining these constituents will not, however, be considered here; the determination of the non-metallic constituents only will be dealt with.

[illegible] of success with this method are given by L. A. [illegible] University, [illegible]

[illegible]

170. The **general plan of analysis** is as follows. For rapid and accurate work a separate portion should be taken for the determination of each constituent.

(1) **Determination of Carbon.** The carbon in cast iron is present both in the free condition ("graphitic carbon") and in combination with the iron ("combined carbon"). It is usually necessary to determine not only the total amount present, but to differentiate between the amounts present in each condition. If the iron be dissolved in acid the uncombined carbon (graphite) remains behind and *the combined carbon is evolved as hydrocarbon.* Solutions of copper salts, however, are capable of dissolving iron, forming ferrous salts and metallic copper, in which no hydrocarbons are evolved, and *both combined carbon and graphite remain behind.*

(a) To determine the **Total Carbon,** the sample is dissolved in a suitable solution of a copper salt and the separated carbon converted into carbon dioxide either by an oxidising solution or by combustion in a stream of oxygen, and weighed as such.

(b) **Graphite,** which remains after the iron is treated with an acid, is determined in a similar manner.

(c) **Combined Carbon** is determined by difference.

(2) **Determination of Sulphur.** The metal is dissolved in bromine-water, the iron precipitated by ammonia, the whole made up to a fixed bulk, filtered, and the sulphur precipitated as barium sulphate in an aliquot portion. Any residue insoluble in bromine-water is fused with sodium carbonate, the fused mass dissolved in water, acidified, and the sulphur therein contained determined as before.

(3) **Determination of Phosphorus.** A separate portion of the metal is dissolved in nitric acid, the oxidation of the phosphorus completed by adding potassium permanganate, and any hydrated manganese dioxide dissolved by the addition of ferrous sulphate. The phosphorus is precipitated as ammonium phosphomolybdate which is filtered, washed and dissolved in ammonia. The solution is then acidified with sulphuric acid, passed through a Jones reductor, and the reduced solution titrated with potassium permanganate (**124**).

(4) **Determination of Silicon.** A separate portion is dissolved in nitric acid and evaporated with sulphuric acid till all water is expelled. The cooled mass is boiled with dilute sulphuric acid to bring iron salts into solution, filtered, and the precipitate ignited. The silica (contaminated with ferric oxide) is weighed and again weighed after treatment with hydrofluoric and sulphuric acids (**98**). The loss in weight represents the silica present and should be calculated to *silicon.*

171. Determination of Total Carbon, using Chromic Acid for its oxidation.

The apparatus employed for converting the carbon separated from the iron into carbon dioxide is similar to that shewn in **90,** but should have a short length of combustion tubing filled with granulated copper oxide (kept in place by coils of copper gauze) inserted between the short condenser C and the first drying tube D. This rests in a short combustion furnace or is heated to redness during the combustion process by several bunsen burners and serves to oxidise to carbon dioxide any hydrocarbons that may be evolved. The apparatus must be set up and tested for leaks as described in **90**.

Place from 1 to 5 grams of the sample (depending on the amount of carbon present) in the flask A (about 250 c.c. capacity) and, by means of the dropping funnel, run in 15 c.c. of a solution of copper sulphate (200 grams of the crystallised salt to 1 litre of water). Allow the solution to act on the iron for a few minutes and then introduce through the funnel [illegible] c.c. of a saturated solution of chromic acid, following it by 135 c.c. of a solution made up of 35 c.c. of the chromic acid solution, [illegible] c.c. of water, 750 c.c. of concentrated sulphuric acid and 340 c.c. of a solution of phosphoric acid of sp. gr. [illegible]. Gradually raise the temperature of the flask, but take care not to hurry the operation, allowing about twenty minutes for the solution to reach its boiling point. At the same time draw a *very slow* current of carbon dioxide-free air through the whole system and boil for about two hours. Aspirate a volume of air through the apparatus equal to about eight times the capacity of the flask A, disconnect the absorption tubes G and H and weigh them. The increase in weight is the carbon dioxide produced by the oxidation of the total carbon in the sample.

---

[1] [illegible]

Solution of the sample in the copper salt may also be effected in a beaker and the residue of carbon afterwards transferred, by the use of a *small* quantity of water, to the flask connected with the absorption apparatus, and oxidised with chromic acid as described.

172. Total Carbon by combustion in Oxygen The iron is dissolved in a solution of copper-potassium chloride which dissolves it more rapidly than copper sulphate. The precipitated carbon is collected on an asbestos filter (*note* (2)), washed, transferred to a platinum boat and converted into carbon dioxide by burning it in a stream of oxygen. Other works should be consulted for a full description of this process.

173. Determination of Graphite A sample of from 1 to 3 grams of the iron is placed in a beaker, nitric acid of sp. gr. 1.2 added in the proportion of 15 c.c. of acid to each gram of iron taken, and, if necessary, the beaker immersed in a vessel of cold water to moderate the action of the acid. When the solution of the iron is complete, only the carbon which was present in the iron in the form of graphite will remain undissolved. Dilute the acid solution and filter this off on to an asbestos filter,(2) free it from iron salts and from silica by successively washing it with hot water, with a hot solution of potassium hydroxide (sp. gr. 1.1) to remove silica, with dilute hydrochloric acid, with hot water again, and finally with alcohol followed by ether. Dry the asbestos filter and residue, place them in the flask of the apparatus used in **171** and determine the carbon by oxidation with chromic acid as described in that paragraph. The carbon may also be determined by burning it in a stream of oxygen as indicated in **172.**

174. Determination of Combined Carbon. This, as stated before, is found by taking the difference between the percentage of total carbon and the percentage of graphite.

175. Determination of Sulphur.(3) Place in a flask 8 c.c. of bromine,(4) and 200 c.c. of water. Add, a little at a time, 5 grams of iron, care being taken to cool the flask after each addition. The reaction is quickly over; when it is complete, boil the solution (in a good draught) to expel the excess of bromine, filter, and wash the residue with water, and finally with a *little* dilute hydrochloric acid. This residue contains part of the sulphur and must be set aside for further treatment. Place in a 500 c.c. graduated flask 130 to 150 c.c. of a 10% solution of ammonia; add to this the filtrate and washings obtained above and make up the volume to the mark. Mix the contents of the flask thoroughly, by pouring back and forth into a clean and dry beaker. Filter out the ferric hydroxide by pouring on to a *dry* filter paper and *do not wash the precipitate.* Take, by means of a pipette, 300 c.c. of the alkaline filtrate and evaporate this in a wide beaker to about 100 c.c. bulk. This evaporation serves the double purpose of concentrating the solution and at the same time expelling much of the free ammonia, so avoiding, later, the formation of undesirable ammonium chloride. (During this evaporation it will be necessary to avoid as far as possible any contamination of the alkaline liquid by sulphurous products of the combustion of coal gas.) To the concentrated solution add 1 drop of dilute hydrochloric acid and 10 c.c. of a 10 per cent. solution of barium chloride. Keep the solution hot till the precipitate settles quickly after stirring, then filter, wash with hot water, ignite and weigh as usual.

To determine the sulphur in the residue, proceed as follows: add to it about 0.5 gram of sodium carbonate, place in a platinum crucible, and burn the filter (using an alcohol lamp in order that no sulphur may be introduced, as would be the case were a gas-flame used). Fuse, and complete the oxidation of the carbon by adding one or two small crystals of potassium nitrate. Dissolve the fused mass in water, filter, slightly acidify with hydrochloric acid, boil the solution, add 5 c.c. of a solution of barium chloride, and treat the precipitated barium sulphate in the manner already described.

---

(1) Fresenius' *Quantitative Analysis*; Clowes and Coleman; Olsen's *Quantitative Analysis*; Phillips' *Engineering Chemistry*. The attention of the student is also drawn to the *Report of the Committee on Standard Methods for the Analysis of Iron*, *Trans. American Foundrymen's Association*, *Philadelphia Convention*, May, 1907, and *Jour. Amer. Chem. Soc.* XXIX, 1376-1476.

(2) [illegible] is ignited at a red heat in a porcelain crucible for half an hour to free it from organic matter. To make a [illegible] a piece of glass tubing about three inches long and three quarters of an inch in diameter is drawn out at one end to form a [illegible] shape the lower half of the tap-funnel shown in **90.** A stout piece of platinum wire is closely coiled and placed resting on [illegible] the narrow part of the funnel [illegible] to protect the filter and precipitate previous to the combustion. Asbestos is roughly ground up with a little water [illegible] assisted if need be by suction, a layer of asbestos is formed on the supporting platinum spiral. On the [illegible] of this is then poured a mixture of water and *finely* ground asbestos which last, after drying, leaves a compact layer of asbestos which [illegible]

(3) [illegible] *Jour. Amer. Chem. Soc.* (1900) XXII, [illegible]

(4) [illegible]

In calculating the results of the analysis, it must be carefully remembered that the sulphur in the barium sulphate resulting from the treatment of the insoluble portion represents [illegible] of the sulphur present, while that obtained from the soluble portion represents [illegible] of the sulphur which originally was in solution.

176. Determination of Phosphorus [illegible] grams of [illegible] steel [illegible] litre flask, and dissolve by adding [illegible] dilute nitric acid (sp. gr. 1.13). Warm the flask gently at first, but when all action is over [illegible]. Through graphitic carbon has separated [illegible] with [illegible] portion of [illegible] to filter the solution into a second flask using as little wash water as possible. To complete the oxidation of the solution add 10 c.c. of a solution of potassium permanganate (1[illegible] grams of salt per litre), and boil till the pink colour is discharged. Add a few crystals of ferrous sulphate [illegible] *[illegible] phosphorus*, [illegible] precipitated hydrated manganese [illegible] dissolved. Cool the solution to about [illegible] and nearly neutralise it by adding ammonia (sp. gr. [illegible]), for which purpose [illegible] should suffice. The remainder of the determination is carried out as described in **124**. Care must be taken to observe the proper temperature and other conditions in order to obtain complete precipitation of the ammonium phosphomolybdate.

177. Determination of Silicon Weigh 1 gram of sample, add 20 c.c. of nitric acid (sp. gr. 1.13); then 5 c.c. concentrated sulphuric acid. Evaporate on a hot-plate until white fumes are driven off. Take up with water and heat till all the ferric sulphate is dissolved. Filter through an ashless filter, with [illegible] filter pump using a cone. Wash once with hot water, once with hydrochloric acid, and then three or four times with hot water. Ignite, weigh, and evaporate with a few drops of sulphuric acid and a few c.c. of hydrofluoric acid. Ignite slowly and weigh. Multiply the difference in weight by [illegible]470[illegible], which will give the amount of silicon in the sample taken.

TECHNICAL METHODS FOR EXAMINING PIG IRON, CAST IRON OR STEEL.[1]

178. Evolution method for the determination of sulphur. Weigh [illegible] grams of drillings into a 300 c.c. Erlenmeyer flask fitted with a cork and delivery tube, the latter bent at right angles [illegible] passing [illegible] tall beaker containing water and about 15 c.c. cadmium chloride solution made by dissolving 10 grams of the salt in [illegible] c.c. of water and adding [illegible] c.c. of concentrated ammonia. Add *gently* to the contents of the flask 50 c.c. of dilute hydrochloric acid (1 to 1) and cork immediately. Place on a hot-plate and when the evolution of gas slackens heat gradually to boiling until only steam is passing over, then disconnect, retaining the delivery tube for use as a stirring rod. To the contents of the beaker add a little starch solution and sufficient hydrochloric acid to dissolve the yellow cadmium sulphide, at the same time running in an excess of $\frac{N}{10}$ iodine solution (**48**, **52**). Titrate the excess of iodine with $\frac{N}{10}$ thiosulphate of sodium and from the amount of hydrogen sulphide found calculate the percentage of sulphur in the sample. (**53** [illegible]).

---

[1] [illegible] with [illegible] **178**.

[illegible] *[illegible]* [illegible] XX[illegible]

[illegible] *Amer[illegible]* [illegible] 1907 [illegible] XXIX [illegible]

[illegible]

[illegible] Com[illegible]

[illegible]

179. [illegible] **175** [illegible] **178** [illegible]

[illegible] Standard Iron Drillings [illegible]

180. Determination of Phosphorus [illegible] precipitated as ammonium phosphomolybdate in the manner indicated in **176** [illegible]

Having obtained the precipitate $(NH_4)_6P_2O_5 . 24MoO_3$, transfer it and the filter paper to the [illegible] the precipitation was made, add about 50 c.c. of water and sufficient standard [illegible] hydroxide solution from a burette to dissolve the precipitate, shaking the flask until this [illegible] with [illegible] nitric acid of similar normality. The difference in the readings is the amount of sodium hydroxide [illegible] equation,

$$2(NH_4)_3PO_4 . 12MoO_3 + 46NaHO = 2(NH_4)_2HPO_4 + (NH_4)_2MoO_4 + 23Na_2MoO_4 + 22H_2O$$

[illegible] gram NaHO [illegible]

[illegible] grams [illegible]

1 gram NaHO = [illegible] grams [illegible]

But as each c.c. of normal NaHO contains 0.04 gram NaHO, therefore 1 c.c. of normal NaHO is [illegible] 0.04 × [illegible] gram phosphorus.

Fifth-normal sodium hydroxide and nitric acid are recommended. The alkali may be standardised [illegible] "Standard Iron Drillings" of known phosphorus content, thus getting [illegible] phosphorus per c.c. for the weight of [illegible]

SPIEGEL-EISEN AND MANGANESE ORE.

181. The determination of Manganese only will be considered. An excellent gravimetric method for technical purposes depends on the fact that ferric hydroxide is precipitated [illegible] salts on the addition of [illegible]

182. Method of Analysis Gravimetric [illegible] dissolved [illegible] and treat the [illegible] **132**

[illegible] when it is not [illegible] to determine the [illegible] must be converted to [illegible] employed **131**.

[illegible]

183. A convenient volumetric method for the determination of manganese is based on the foregoing separation of iron and manganese by the use of zinc oxide and on the fact that manganese sulphate or nitrate reacts, in hot dilute neutral solution, with potassium permanganate, in a manner which may be expressed by the following equation:

$$3Mn(NO_3)_2 + 2KMnO_4 + 2H_2O = 2KNO_3 + 4HNO_3 + 5MnO_2$$

Taking 55 as the atomic weight of manganese, 316 grams of permangate are thus equivalent to 165 grams of manganese. As a solution of permanganate that is decinormal when used for the titration of iron contains 3.16 grams per litre (**33**), 1 c.c. of such a solution will be equivalent to $\frac{165}{100000}$ grams manganese, namely .00165 grams.[114]

Proceed as described above for the gravimetric determination, (**182**), up to the point where, the iron having been separated and the solution filtered, an aliquot part is to be taken for the determination. For this purpose it will be sufficient to take 100 c.c. of the filtrate. Place this in a porcelain casserole,[115] add 200 c.c. of water and boil. While still almost boiling, run in a decinormal solution of potassium permanganate, stirring very vigorously the whole time. If the permanganate is run in rapidly, a more accurate result is likely to be obtained, and it is generally best to make a rough determination on one portion of 100 c.c. to learn how much may be added with rapidity and safety. *The brown precipitate will only settle well if thoroughly stirred* (or rather beaten, as though beating an egg) while it is forming. The end-point is reached when the supernatant liquid is faintly pink.

This method is extremely rapid and convenient, though some practice is required in judging the end-point. It is not, however, so accurate as the gravimetric method, since there is always a certain amount of permanganate decomposed through the catalytic action of hydrated manganese dioxide upon it. Its inaccuracy is reduced to a minimum if the solution of potassium permanganate used is standardised on a spiegel, the composition of which is accurately known, instead of upon iron. Should the manganese be present as a chloride (through decomposing the manganese ore with hydrochloric acid, for instance), it must be evaporated with a slight excess of sulphuric acid till all hydrochloric acid has been expelled before this method can be applied.

TOURMALINE.

This complex mineral may be considered as a silico-borate of aluminium and magnesium. The determination of boron presents considerable difficulty, and will be alone considered here. The method employed depends on two important facts, (1) the ready formation and low boiling point of methylic borate—$B(OCH_3)_3$—and (2) the ease with which free boric acid may be titrated with a solution of sodium hydroxide, using phenolphthalein as an indicator, *when a large excess of glycerol is present.*

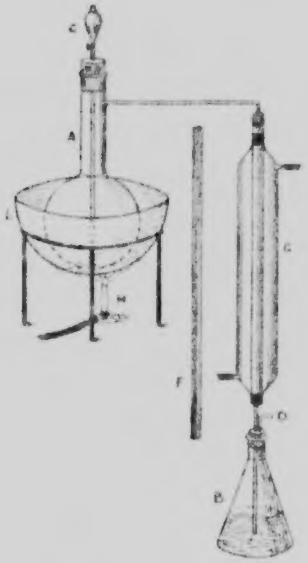
184. Determination of Boron as Boric Acid. Fuse 1 gram of finely ground tourmaline in a platinum crucible with 5 or 6 times its weight of potassium and sodium carbonates. Avoid, if possible, the use of a blowpipe. Chill the fused mixture somewhat quickly and when cold roll the crucible gently between the fingers. The greater part of the mass will now

---

[114] The manganese equivalent of any solution of permanganate whose iron value is known [illegible] 0.2946. This figure is found as follows: from the above equation it is seen that 3 × 55 grams manganese are oxidised by 316 grams [illegible] (**34**) it is evident that 10 × 56 grams iron are also oxidised by 316 grams permanganate. So if 1 c.c. of the standard permanganate used is equivalent to x grams of iron, the manganese equivalent of that solution is found from the proportion 10 × 56 : 3 × 55 :: x grams iron : y grams manganese,

i.e., y grams manganese = [illegible] = 0.2946 [illegible]

[115] Some workers prefer to make this titration in a conical flask with a tightly-fitting rubber stopper. In that case the flask is re-stoppered and vigorously shaken after each addition of permanganate. The eff[illegible]



drop from the crucible without difficulty. Having fitted up the apparatus shown in the figure, transfer the detached mass resulting from the fusion to the flask A which is placed in a bath of glycerine, E. F is a sheet of asbestos to protect the condenser G from the heat of E and of the burner. Rinse the crucible with sulphuric acid (1 part concentrated acid to 1 part water), add these rinsings to the contents of the flask, with as much more acid as may be necessary to strongly acidify the whole and to bring it to a pasty condition. Into the receiving flask B run 25 c.c. of deci-normal solution of sodium hydroxide. Let the condenser tube dip about 1 inch below the liquid. To the contents of the flask A add 10 c.c. of pure methyl alcohol, close the stopcock C, and raise the temperature of the glycerine bath till the distillate passes over freely. When the rate of distillation slackens, attach the tube D to a filter pump, and draw a slow current of air through the apparatus, regulating its speed by the stopcock C. Interrupt the air current, and add other 10 c.c. of methyl alcohol. Repeat this operation, alternately adding methyl alcohol and completely drawing it over (with the methylic borate formed) by a current of air, till 60 c.c. of methyl alcohol in all has been used. Then disconnect the flask B, run in 25 c.c. of deci-normal hydrochloric acid (thus exactly neutralising all the alkali present, and liberating all the boric acid), add 100 c.c. of glycerol and a few drops of phenolphthalein, and titrate with a deci-normal solution of sodium hydroxide, till a pink colour appears.(116 and 117)

The principal reactions involved may be expressed by the equations:—

$$Na_2O.B_4O_7 + H_2SO_4 + 2H_2O = Na_2SO_4 + 2B(OH)_3$$

$$B(OH)_3 + 3CH_3OH = B(OCH_3)_3 + 3H_2O$$

$$B(OCH_3)_3 + 3H_2O \text{ (in presence of alkalies) } = B(OH)_3 + 3CH_3OH$$

and for final titration,—$2B(OH)_3 + 2NaOH = 4H_2O + Na_2O.B_2O_3$.

---

(116) See also *Jour. Soc. Chem. Ind.*, XXV., 1906, p. 237; and *ibid.*, XXVI., 1907, p. 803.

(117) *The following analysis of a tourmaline from New Jersey is given by G. W. Sargent in the Jour. Amer. Chem. Soc.*, XXI., p. 874—SiO_2, 33.72; B_2O_3, 10.06; Al_2O_3, 25.88; Fe_2O_3, 1.82; FeO, 3.25; CaO, 0.92; MgO, 14.07; K_2O, 0.20; Na_2O, 2.52; Loss on ignition 1.80 per cent.

APPENDIX.

International Atomic Weights, 1911.

		0 = 16.
Aluminium	Al	27·1
Antimony	Sb	120·2
Argon	A	39·88
Arsenic	As	74·96
Barium	Ba	137·37
Bismuth	Bi	208·0
Boron	B	11·0
Bromine	Br	79·92
Cadmium	Cd	112·40
Cæsium	Cs	132·81
Calcium	Ca	40·09
Carbon	C	12·00
Cerium	Ce	140·25
Chlorine	Cl	35·46
Chromium	Cr	52·0
Cobalt	Co	58·97
Columbium	Cb	93·5
Copper	Cu	63·57
Dysprosium	Dy	162·5
Erbium	Er	167·4
Europium	Eu	152·0
Fluorine	F	19·0
Gadolinium	Gd	157·3
Gallium	Ga	69·9
Germanium	Ge	72·5
Glucinum	Gl	9·1
Gold	Au	197·2
Helium	He	3·99
Hydrogen	H	1·008
Indium	In	114·8
Iodine	I	126·92
Iridium	Ir	193·1
Iron	Fe	55·85
Krypton	Kr	82·9
Lanthanum	La	139·0
Lead	Pb	207·10
Lithium	Li	6·94
Lutecium	Lu	174·0
Magnesium	Mg	24·32
Manganese	Mn	54·93
Mercury	Hg	200·0
Molybdenum	Mo	96·0
Neodymium	Nd	144·3
Neon	Ne	20·2
Nickel	Ni	58·68
Nitrogen	N	14·01
Osmium	Os	190·9
Oxygen	O	16·00
Palladium	Pd	106·7
Phosphorus	P	31·0
Platinum	Pt	195·0
Potassium	K	39·10
Praseodymium	Pr	140·6
Radium	Ra	226·4
Rhodium	Rh	102·9
Rubidium	Rb	85·45
Ruthenium	Ru	101·7
Samarium	Sa	150·4
Scandium	Sc	44·1
Selenium	Se	79·2
Silicon	Si	28·3
Silver	Ag	107·88
Sodium	Na	23·00
Strontium	Sr	87·62
Sulphur	S	32·07
Tantalum	Ta	181·0
Tellurium	Te	127·5
Terbium	Tb	159·2
Thallium	Tl	204·0
Thorium	Th	232·0
Thulium	Tm	168·5
Tin	Sn	119·0
Titanium	Ti	48·1
Tungsten	W	184·0
Uranium	U	238·5
Vanadium	V	51·06
Xenon	Xe	130·2
Ytterbium (Neoytterbium)	Yb	172·0
Yttrium	Y	89·0
Zinc	Zn	65·37
Zirconium	Zr	90·6

INDEX.

The numbers refer to Paragraphs; Those in brackets to the foot-notes.

ACETIC acid, decinormal 19, 20
  determination of, 28
Acidimetry, 28
Alkalies,
  determination of, 64, 65
  " " in Clay, 113
Alkalimetry, 21, 27
Aluminium,
  determination of, 79
  " " in Limestone, 95
  " " in Clay, 108
  " " in Haematite, 131
Ammonia,
  direct determination of, 27
  determination of, by titrating back 29, 70
Ammonium oxalate, determination of, 42
Analysis, gravimetric, 1, 72 et seq.
  " volumetric, 3, 21-71
Antimony,
  determination of, by Iodine, 55
  " " in Pyrites, 162-166
Arsenic,
  determination of, in Copper Matte, 147
  " " in Pyrites, 163
  " " by Iodine, 54
Arsenious oxide, standard solution of (30)
Asbestos filter, (99)
Ash in Coal 137
Atomic weights, table of, *Appendix.*

BARIUM, determination of, 82
Bichromate,
  determination of Iron by, 44-46
  indicator for use with, 43
  standard solution of, 43
  standardisation of, 47
Bleaching-Powder, determination of available Chlorine in, 66-68
British Thermal Unit, 141a
Burettes, 5, 8
  " reading, 9

CALCIUM,
  determination of, 85
  indirect determination of, 41
  determination of, in Clay, 112
  " " in Haematite, 133
  " " in Limestone, 96
Calorie, 141a
Calorimeter, 141a
Carbon,
  combined, determination of, in Iron 170, 171
  total, " " " 171
  fixed, " " in Coal 139
Carbon dioxide, determination of, 88-90
Carbonate,
  determination of an insoluble, 30, 88-90
  of an alkali, determination of, in presence of a hydroxide, 26
Cast Iron, technical method of analysis, 178-180
Chlorates, determination of, 64
Chlorine,
  determination of, by Iodine and Thiosulphate 59
  volumetric determination of, by Silver Nitrate, 63
  determination of, in Bleaching Powder, 66-68
Chromium, determination of, 80
Clay, analysis of, 103
  " composition of, 103

The numbers refer to Paragraphs; Those in brackets to the foot-notes.

Coal,
  analysis of, 135
  ash in, 137
  calculation of analytical results, 141
  calorific value of, 141a
  coking properties of, 141a
  fixed carbon in, 139
  moisture in, 136
  sulphur in, 140
  volatile combustible matter in, 138
Copper,
  gravimetric determination of, 81
  determination of, by Iodine and Thiosulphate, 61
  determination of, in Pyrites, 157
  " " in Copper Matte, 149
  electrolytic determination of, 142
  and Iron, determination of, when mixed, 87
Copper Matte, 142
Cylinders, graduated, 5

EVAPORATION of liquids, 73

FACTORS, 2, (4)
Ferric salts,
  gravimetric determination of, 78
  determination of, by permanganate 36, 37
  " " by bichromate, 45, 46
Ferrous salts,
  gravimetric determination of, 78
  determination of, by permanganate 35-37
  " " by bichromate, 44-46
Filter, asbestos, (99)
Filtration, 75
Flasks, graduated, 5
  " " reading, 9
Fusion mixture, for silicates, (60)
  " " pyrosulphate, 109

GRAPHITE, determination of, in Iron, 173
Gangue,
  determination of, in Copper Matte, 145
  separation of Lead from, 154

HAEMATITE, analysis of, 118-134
Hardness of water, determination of, 31
Hydrochloric acid, decinormal, 19, 20, 23, (1)
  " " determination of, 28, 63
Hydrogen sulphide, 53, 58

INDICATORS, 21-22, 43, 62, 66
Iron,
  analysis of, 169
  and Aluminium, separation of, 109-111
  and Copper, determination of, when mixed, 87
  and Nickel, separation of, 159
  determination of, in Clay, 108-111
  " " Copper Matte, 150
  " " Haematite, 119-120
  " " Limestone, 95
  ferrous, determination of, in Clay, 117
  separation of, as basic acetate, 131
Iodine,
  determination of, by thiosulphate, 51
  determinations by direct titration with, 52 et seq.
  indirect determinations by means of iodine and thiosulphate 58-61
  standard solution of, 48-49

INDEX.

The numbers refer to Paragraphs; Those in brackets to the foot-notes.

JONES reductor, (75)

KAOLIN, Chinese, analysis of, (81)
Kilogram-calorie, (87a)
Kjeldahl, determination of Nitrogen by, 69-71

LEAD,
  determination of, 83
    " " in Copper Matte, 148
Limestone, analysis of, 91

MAGNESIA Mixture, (60)
Magesium,
  determination of, 84
    " " in Clay, 112
    " " in Haematite, 133
    " " in Limestone, 97
Manganese,
  determination of, in Haematite, 132
    " " in minerals 132
  gravimetric determination of, in Spiegel Eisen, 182
  volumetric method for determination of, 183
  ore, 181
Mohr's salt, 78
Moisture in Coal, 136
Molybdate, ammonium, preparation of, (67)

NEUTRALISATION, 11
Nickel,
  determination of, in Nickel Steel, 167-168
    " " in Pyrites, 158
  separation of, from Iron, 159
Nickel Steel, 167
Nitrates, determination of, 64
Nitrogen, determination of, 69
Normal solutions, 16, 17
Normality of a solution, 23, (7)

OXALATES, determination of, 40, 41
Oxalic acid, determination of, 39
Oxidation, 12
  " analytical methods based on, 32

PARR'S Calorimeter, 141a
Permanganate,
  standard solution of, 33
  standardisation of, 38
  determination of Iron by, 35-37
    " " Oxalic acid by, 39
    " " Oxalates by, 40
Phosphoric acid, determination of, 86
Phosphorus,
  determination of, in Iron, 176
    " " in Iron and Steel, 180
    " " in Haematite, 123, 124, 129
    " " in Limestone, 100
Pig-iron, technical method of analysis, 178-180
Pipettes, 6
  " reading, 7
Platinum vessels attacked during fusions (74)
Potassium,
  determination of, in Clay, 114
  hydroxide, determination of, 23
  hydroxide and carbonate when mixed, determination of, 26

The numbers refer to Paragraphs; Those in brackets to the foot-notes.

Precipitates,
  drying, 76
  ignition of, 77
  removing from paper, 78
  washing, 75
    " convenient arrangement for (71)
Precipitation, methods, 3, 4, 62, 74
  " volumetric methods based on, 62
"Preventive solution," (83)
Pyrites, 155

REDUCTION, 12
Reductor, Jones, (75)

SILICA,
  determination of, in Clay, 106, 107
    " " in Haematite, 122, 128
    " " in Limestone, 98
Silicon, determination of, in Iron, 177
Sodium carbonate, determination of 24
Solution, preparing a, 73
Solutions,
  standard, 15
  decinormal, 19, 20
    " Acetic acid, 19, 20
    " Arsenious oxide, (53)
    " Bichromate, 43, 44
    " Hydrochloric acid, 19, 20, 23, (1)
    " Iodine, 49
    " Permanganate, 33, 34
    " Potassium hydroxide, 19, 20
    " Silver nitrate, 62
    " Sodium carbonate, 19, 20, 23, (1)
    " Sulphuric acid, 19, 20, 23, (1)
    " Thiosulphate, 50
  normal, 16, 17, 18
  normality of, 23, (7)
Spiegel-Eisen, 181
Standard solutions, 4, 15
Starch-paper, 66
Steel, technical method of analysis, 178-180
Sulphites, determination of, 56, 58, 60
Sulphur,
  determination of, in Coal, 140
    " " " Copper Matte, 153
    " " " Haematite, 125
    " " " Iron, 175
    " " " Iron and Steel, 178
  evolution method for determining, 178
Sulphuric acid, decinormal, 23, (1)
  " determination of, 28, 82
Sulphur dioxide, determination of, 56, 58, 60

TEMPERATURE, rough test for, 39
Thiosulphate of sodium, standard solution of, 50
Tin, determination of, by Iodine, 57

VOLATILE combustible matter in Coal, 138

WATER, determination of combined, 115
Water, determination of "hardness" of, 31

ZINC,
  determination of, as oxide, 152
    " " electrolytically, 151
    " " in Copper Matte, 151